

RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XI

NUMBER 1



January, 1938

Published under the Auspices of the
RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY

MICRONEX BEADS

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RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues (\$2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division upon payment of \$4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given RUBBER CHEMISTRY AND TECHNOLOGY.

Rubber Division Activities

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Rubber Technology Conference

To Be Held in London under the Auspices of the Institution of the Rubber Industry, May 23-May 25, 1938

For several years the Council of the Institution of the Rubber Industry has endeavored to arrange a Conference for the purpose of bringing together a representative gathering of rubber technologists from Overseas. It is with great pleasure, therefore, that the Council announces that the Rubber Division of the American Chemical Society is willing to support such a Conference, which is being arranged to be held in London in May, 1938.

Cordial invitations are extended to rubber technologists in all countries, as it is felt that many will be glad to take this opportunity of meeting their colleagues in the Industry.

It is intended that matter submitted to the Conference shall be original, and definitely practical in character. Not only will there be the opportunity for those attending to discuss matters of mutual interest, but it is hoped to provide for visits of inspection to rubber works, and to the leading scientific and educational Institutions.

Further, the Conference Organisation Committee will appoint a General Reporter for each section of the Conference, whose duties will include the preparation of a general review of papers submitted, and the direction of the attention of the meeting to points which might most usefully be discussed.

Copies of papers and the General Reports will appear as long in advance of the Conference as possible, thus conserving the major portion of Conference time for profitable discussion.

Technical Program

The appended Program is set out to give the scope of the Conference, not necessarily the titles of papers.

In order that the Conference may meet with a definite object in view, the Council has decided that the principal part shall be a Symposium on Methods of Improving and Evaluating the Durability of Rubber, and contributions in Part I of the Program dealing with aspects of this field will be particularly welcome.

To avoid confining the Conference within too narrow limits, however, and to provide for the interests of those whose work is not directly concerned with the subject of the Symposium, the second part of the program will be devoted to general subjects within the scope set out below.

Part I.—Methods of Improving and Evaluating the Durability of Rubber

1. Manufacturing conditions, including compounding.
2. Uses of "synthetic rubbers" and allied plastics.
3. Testing methods, including chemical, physical, performance, and accelerated aging tests.

Part II.—General Subjects

1. Chemistry and physics of latex and rubber.
2. Technology of latex and rubber.
3. Rubber derivatives and their uses.
4. Raw materials of the rubber industry.
Compounding ingredients, solvents, varnishes and finishes, fibers and textiles.
5. Manufacture of particular goods.
Tires, belting, electric cables and insulation, footwear, sports goods, and toys, hose, general mechanicals, roads and flooring, surgicals, textile-rubber goods, sponge and cellular rubber, hard rubber.
6. Machinery and appliances, steam and heat.
Water, automatic control, layout, transport, packing, storage, maintenance.
7. Organisation and administration.
Technical education, production planning and efficiency, safety and welfare, costing, marketing, economic problems.

Instructions for Authors of Papers

1. All papers will be printed in Great Britain under the supervision of the Council of the Institution of the Rubber Industry and will be available prior to the Congress.

After the Conference the papers, together with the discussions thereon, will be published by the Council in one or more volumes, entitled:

TRANSACTIONS of the INSTITUTION of the RUBBER INDUSTRY CONFERENCE LONDON, 1938

2. The Council will accept only original papers that have not hitherto been published. Such papers should avoid too great detail and should deal primarily with problems of general importance to the rubber industry; they should contain a general review of the development, tendencies, and problems arising in connection with the technical branch concerned and should include, when possible, a list of the problems calling for scientific research. The value of the papers will in most cases be enhanced by the addition of a bibliography.

3. Papers should preferably not exceed 5000 words in length. Preferably they should be presented in English, and should be accompanied by a summary and conclusions, not exceeding 500 words in length. Papers shall not contain any matter which could be considered to be of an advertising nature. Papers presented shall not be published elsewhere prior to the Conference.

4. With the exception of mathematical symbols and formulas, which should be written by hand, the text of the papers should be typewritten with double spacing, using one side of the page only, and two copies should reach the Secretariat of the Rubber Technology Conference *not later than March 31, 1938*.

5. Footnotes intended for printing in the text should be given at the foot of the page on which the reference occurs. Alternatively they may be inserted in the typewritten copies immediately below the line to which they refer, and between it and the next following line, provided they are written in ink of a different color,

6. The dimensions of reproductions of photographs, drawings, etc., will not exceed 4 inches by 7 inches (10 centimeters by 18 centimeters). Titles should be typewritten on the back of each photograph or drawing. The number of illustrations should be kept as low as possible, and the Conference Committee reserves the right to ask for payment at cost for any illustrations above a reasonable maximum. Authors are particularly requested to supply fully descriptive captions with each illustration.

7. Photographs should be clear prints suitable for reproduction without retouching.

8. Drawings should be made with jet black ink on white paper, lettering to be in plain block letters. Line drawings should be prepared at about twice the size (linear) of the drawing as it will appear in print. Unless prepared by a draughtsman, all letters, shading, etc., should be drawn lightly in soft lead pencil as a guide to the engraver. If sectional or squared paper is used, only that with faint blue ink lines should be selected.

9. The symbols used in papers should, as far as possible, be those internationally recognized. Each author is particularly requested to state clearly the units employed in his paper, *e. g.*, ton (2000 lbs.) or ton (2240 lbs.), and gallon (volume of 8.33 lbs. of water) or gallon (volume of 10 lbs. of water), etc.

10. Copies of Papers and General Reports will be issued as long in advance of the Conference as possible. Official Delegates will be supplied on request with copies free of cost. Authors of papers will be supplied with five copies of their papers and one copy of the General Report dealing with the Section in which their paper appears, free of cost. Members of the Congress will be given the opportunity of purchasing such copies as they require at a cost which will be announced in a price list.

The Committee would be glad to hear as soon as possible from those contemplating submitting papers to the Conference.

All communications to be addressed to—

The Secretary

Institution of the Rubber Industry,
12, Whitehall, London, S. W. I.

Tenth International Congress of Chemistry

The Tenth International Congress of Chemistry will be held at Rome, Italy, from May 14 to 21, 1938, inclusive. The scientific meetings will be in the new "University City" on May 16, 17, 18, and 20. Part of May 15 and 17 and all of May 19 are open for organized excursions in and out of Rome. There will be a grand closing banquet on May 21. Papers on practically all phases of pure and applied chemistry (including rubber, according to the program), are to be presented at the meetings, and papers by American rubber chemists will doubtless be extremely welcome.

This Congress may be of interest to some American Rubber Chemists because it is to be held during the week preceding the **Rubber Technology Conference** in London, on May 23 to 25. It is therefore possible to attend the International Congress in Rome, with all its intellectual and social benefits, and then to go directly to London in ample time for the Rubber Conference.

More detailed information will gladly be furnished by the Editor of **RUBBER CHEMISTRY AND TECHNOLOGY** to anyone who is interested in attending the **International Congress** at Rome, either as an inactive or as an active participant.

New Books and Other Publications

The Chemistry and Technology of Rubber, Edited by C. C. Davis and J. T. Blake. (American Chemical Society Monograph Series No. 74). Reinhold Publishing Corp., New York; Chapman & Hall, Ltd., London, 1937. 941 pp. \$15.00.

In his preface the Editor states that this book represents an effort to correct a fundamental shortcoming of previous books on the chemistry of rubber, namely, that "no one rubber chemist has been able to write authoritatively, comprehensively, and at the same time critically, on the vast store of knowledge which has accumulated."

The first steps towards the production by the American Chemical Society of a book of composite authorship were taken as early as 1928. The book now presented comprises the contents of two symposia held in 1933 and 1934, together with further chapters contributed by some twenty other authors. Altogether thirty-nine leading rubber scientists and technologists, both American and European, have contributed chapters dealing with the particular branches of the subject on which they have specialized knowledge and experience.

The result of this coöperative effort is the most comprehensive, authoritative, and up-to-date account of the science and general technology of rubber in the English language. The subject-matter comprises raw rubber, its composition, physical properties, mastication, and plasticity; the rubber hydrocarbon; behavior of raw and vulcanized rubber towards solvents; vulcanization theories and phenomena, vulcanization without sulfur, accelerators, and theories of acceleration; physics of vulcanized rubber; fillers and reinforcing agents; aging, autooxidation, and antioxidants; electrical properties of rubber; latex, its properties and applications; hard rubber; chemical derivatives of rubber; synthetic and substitute rubbers; gutta-percha and balata; reclaim; practical compounding; analysis and physical testing of rubber; and literature on the chemistry of rubber. In view of the inclusion of the word "Technology" in the title it should be pointed out that general rubber manufacturing processes, machinery, auxiliary materials such as solvents and textiles, and the production of individual types of rubber articles are in general not discussed; information on manufacturing processes is, however, given in certain specialized fields, such as latex and gutta-percha. While speaking of the title it may be mentioned that the words "Chemistry and Technology" scarcely do justice to the important part played by physical—as distinct from chemical—properties and phenomena in the science of rubber.

With the exceptions noted above, the various aspects of rubber science and technology are well covered by the twenty-six chapters, with perhaps some emphasis on the scientific side. The treatment of the subject-matter is generally thorough and lucid. As is perhaps inevitable in a book of composite authorship, the amount of detailed information quoted from original papers varies rather considerably from one chapter to another, a few of the authors having perhaps relied rather too much on referring the reader to the original sources for important data. The chapters are, in the great majority of cases, provided with copious references to original papers, often extending to hundreds of items; there are, on the other hand, one or two cases, *e. g.*, Chapter VIII on the History and Use of Accelerators, where the number of references hardly seems commensurate with the importance of the subject. The literature references are conveniently listed at the end of each chapter. A small improvement which may be suggested here is to make these lists uniform in style throughout the book; at present some are in alphabetical order of authors, some without authors' names, some classified by subject, etc.

In addition to the individual reference lists for each chapter, there is a complete author index and a very full subject index; a minor criticism of the latter is the occasional use of the word "rubber" without a clear indication as to whether raw or vulcanized rubber is referred to.

The adoption of the multiple authorship system and the fact that the book has been built around the papers comprised in two symposia have not unnaturally led to some overlapping and duplication. This occurs more particularly among chapters dealing with closely related subjects, *e. g.*, chemistry and physics of raw rubber (Chapters II, III, IV, and V), and oxidation, aging, and antioxidants (Chapters XII, XIII, and XIV). That such duplication is, in the circumstances, almost unavoidable is clearly recognized by the Editor, who points out that it may really be of advantage in giving the reader different points of view on one and the same subject. To the student seeking a well-balanced picture of the present state of knowledge on a subject, this feature undoubtedly is a valuable one. On the other hand, those who use the book as a reference work may find it troublesome to have the same data presented in two or three places. There are, moreover, one or two instances where apparently contradictory statements appear, *e. g.*, on pp. 563 and 718 concerning the composition and the identity or otherwise of Pernax and Gutta-Gentzsch; pp. 121 and 717 concerning the identification of the *cis* and *trans* forms of the caoutchouc molecule with rubber and gutta, respectively, or *vice versa*; and pp. 568 and 763-764 concerning the effect of combined sulfur content on insulation resistance.

It is not intended here to attempt to discuss the relative merits of the various chapters. Reference must be made, however, to certain chapters which present exceptionally good surveys and summaries of difficult and controversial subjects, such as Chapter VI on Theories and Phenomena of Vulcanization, Chapter X on the Physics of Vulcanized Rubber, Chapter XI on Fillers and Reinforcing Agents, and Chapter XIII on Autooxidation and Deterioration by Oxygen. Chapter XXIII on Practical Compounding presents an admirable compilation of useful information on a subject that is usually very inadequately treated in books on rubber. A valuable feature of some of the chapters dealing with theoretical topics on which there has been much speculation is the presentation of a summary of the definitely established facts in the field under review. In this connection it may be added that "The Chemistry and Technology of Rubber" performs a valuable service not only in telling us what is known, but in bringing home to us how little real knowledge we possess on such important matters as the mechanism of reinforcement, to quote one striking instance.

The chapter on "Vulcanization without Sulfur" will be read with interest on account of the explanations given by the author (Ostromislensky) for the failure of other workers to repeat his results.

A few of the chapters, *e. g.*, those dealing with "Hard Rubber" and the "Properties of Latex" might with advantage have been made fuller in subject-matter and treatment. In certain chapters, too, the technologist, as distinct from the scientist, may find the practical side of the subject less fully discussed than the theoretical; this applies, for instance, to the discussion of swelling of vulcanized rubber (Chapter V) and synthetic and substitute rubbers (Chapter XX).

The contributors of the various chapters have evidently taken considerable care to ensure the accuracy of the enormous mass of facts presented, and so one very rarely finds statements that can be questioned. A fairly careful scrutiny has only brought to light a few, such as: "hard rubber does not swell appreciably" [in organic liquids] (p. 187); vulcanizates do not usually give S-shaped (autocatalytic) oxidation curves (p. 451; cf. p. 531); sulfur "is almost inert with respect to the

autooxidation of rubber" (p. 514); bleaching of Prussian blue during vulcanization "is associated with steam" (p. 549); measurement of hardness on thin specimens "is not permissible" (p. 811); the bromine method of determining free sulfur includes the sulfur in organic compounds (p. 862).

Omissions appear to be few and relatively unimportant, *e. g.*, absorption spectrum of rubber, optical properties of vulcanized rubber, theory of indentation hardness tests; reliable information on the German Buna rubbers, which are not mentioned in the book, is perhaps of too recent date to have become text-book matter. For the European reader the lists of accelerators and antioxidants, with trade names, on pp. 302-303 and 434-435, might with advantage have been extended to include more products of non-American origin.

The printing and proof-reading have evidently been carried out with great care, as there are extremely few misprints. The following may, however, be noted: "Tetch," for "Petch" (p. 287); "2.50," for "250" (p. 810, "Pusey-Jones Plastometer" column); "Shacklock," for "Shacklock" (p. 149); temperature is omitted from the top curve in Fig. 1, p. 63; in the equation on p. 166 an "equals" sign should be inserted between dv/dy and the expression in brackets.

In drawing attention to a number of minor defects it has not been the intention in any way to disparage the efforts of the contributors and the editors of "The Chemistry and Technology of Rubber," who have conscientiously and painstakingly carried out a work of outstanding value. It is hoped rather that these comments may be of some constructive value in the preparation of subsequent editions. "The Chemistry and Technology of Rubber" is, indeed, such an excellent book that one feels it to be worth while taking some little trouble to help to bring it even nearer to perfection.

The Rubber Division of the American Chemical Society is to be congratulated on having been instrumental in producing an invaluable summary of the present state of knowledge of the science and technology of rubber, enhanced by a series of critical discussions on many important problems by outstanding figures in rubber science. As such, this book cannot fail to be of great service in promoting the scientific study of rubber and the application of the results to technical development. The large amount of thought-provoking matter contained in its many hundreds of pages proves, indeed, to be one of the greatest difficulties for the reviewer, for on almost every page some interesting fact or point of view tempts the mind to wander off on a fascinating line of thought.

For those familiar with the American Chemical Society Monograph series, it is scarcely necessary to add that the paper, printing, and binding of this latest addition to the series are fully worthy of a book which may be regarded as America's greatest contribution to the literature of rubber. [J. R. SCOTT.]

Rubber Red Book. 1937 Edition. Directory of the Rubber Industry. With Annual Bibliography of Rubber Literature for 1936. The Rubber Age, 250 West 57th St., New York. 6 × 9 in. 370 pp. Paper \$2.00; cloth \$3.00.

This combined directory and bibliography of the American rubber industry is the best that has yet appeared. An extension and enlargement of information contained in the "Annual Bibliography of Rubber Literature," published in 1936, the book consists of two main departments. The first is a complete and detailed directory, both alphabetical and geographical, giving the address, chief products, and personnel of rubber manufacturers in the United States and Canada. In addition, rubber machinery and its makers, brand names and sources of supply of chemicals and compounding materials, fabrics, and crude and reclaimed rubbers are listed. Dealers in crude and scrap rubber are catalogued, and also consulting engineers and

technologists. An entire section is devoted to materials for compounding latex. A valuable feature is an article by R. J. Noble, describing practical problems and the technic employed in this increasingly important phase of the rubber industry.

The second portion of the book is a complete bibliography of rubber literature for 1936, compiled by D. E. Cable. This is preceded by an alphabetical list of many scientific, technical, and trade journals. The bibliography is carefully grouped according to subjects, so that any article may be located with a minimum of time and effort. Incidentally, there seems to be no good reason for devising a new set of abbreviations for these journals instead of employing the accepted standard abbreviations of the American Chemical Society. It is to be hoped that this annual bibliography may continue, as it should become almost indispensable for research workers in rubber and its allied fields.

It is evident that considerable care has been taken to maintain the high standard of accuracy and utility set by the previous edition. Such advertising as the book contains is well distributed and conservative. This "Red Book" should fill an important need in the library of every industry wherein such information is desired. [G. G. HAWLEY.]

Report of the Symposium on Rubber. The India-Rubber Journal. London, 1937.

At the end of 1936, on the occasion of the opening of the Laboratory of Colloid Chemistry of the Higher Technical School at Delft, there was held a Symposium on Rubber, at which important papers were presented. Translations of these papers have already been published in various issues of the *India-Rubber Journal*, and now these papers by eminent specialists have been combined under a single cover. The book is published in excellent form, and comprises the following communications:

Hevea brasiliensis as a producer of rubber. G. Van Iterson.

Latex and coagulum. O. De Vries.

The chemical structure of natural rubber and of different varieties of artificial rubber. J. P. Wibaut.

X-ray spectrography of soft natural rubber. J. R. Katz.

Chemical aspects of vulcanization. A. van Rossem.

Applications of latex. J. G. Fol.

The structure of the macromolecule of rubber and the elastic properties of rubber. I. R. Houwink.

The relation between elasticity and plasticity of rubber. J. Hoekstra.

New processes in the treatment of raw rubber. C. J. Rondberg.

Electric properties of technical rubber mixtures. A. J. Wildschut. [*La Revue générale du caoutchouc.*]

The Accelerated Vulcanization of Rubber. T. Grenness. Levin & Munksgaard, Copenhagen, 1937. Price 10 crowns.

This English edition is a translation from the Danish, the original of which was presented as a thesis for a doctorate degree at the Royal Technical College at Copenhagen. The author calls attention to the considerable increase during the last seven years in our knowledge of the chemical structure and formation of rubber, in contrast to the slight progress in explaining the vulcanization process, particularly the effects and reactions of accelerators. In his work the author studies some of the problems of vulcanization, in the course of which work he used various accelerators, chiefly dithiocarbamates and thiuram sulfides. He has sought by means of a large number of experiments to explain the reactions of these substances, both with sulfur and with activators and retarders. The author, who has already

written a memoir on his "Investigations of the application of bone glue in rubber mixtures," has included in the present volume, in the summary of his experiments and their practical application, the results of this study.

Following a résumé of various theories on the reactions of accelerators, the author gives a summary of his physical and chemical experiments, including:

1. The technic employed (general remarks; measurement of the resistance to tearing).

2. Experiments with dithiocarbamates and thiuram sulfides.

3. Influence of certain metallic oxides on vulcanization with thiuram disulfides.

4. The effects of glue and of water on vulcanization and vulcanized products.

The final chapter is devoted to the practical application of the results, in particular to the use of glue in rubber mixtures. This work is a valuable contribution to the study of rubber, both from the theoretical and from the practical point of view. [*Le Caoutchouc et la gutta-percha.*]

Polymerization. Robert E. Burk, Howard E. Thompson, Archie J. Weith, and Ira Williams. Published by Reinhold Publishing Corp., New York, N. Y. 1937. Cloth, 6 × 9 inches. 312 pages. Index. Price \$7.50.

This book (American Chemical Society Monograph No. 75), presents the theoretical aspects of polymerization, a type reaction of broad interest, and its applications in the fields of rubber, synthetic resins, and petroleum. The authors have succeeded in arranging the material in a way which provides an up-to-date and accurate impression of the subject. The work is timely, as recent industrial advances in this field are proceeding at a lively rate. No attempt, however, has been made to produce a complete encyclopedia on the subject.

About half of the book is devoted to theory, which stresses the rate and mechanism of polymerization reactions as related to the molecular structure of the starting materials and the presence of catalysts. Considerable detail on polymer structure is given in the chapters on the rubber and synthetic resin industries. Listed in Chapter III in tabular form are 838 different combinations of catalysts and substances to be polymerized, giving in most cases the reaction conditions, products, and literature reference. This arrangement is according to catalyst, but a cross-index lists the substances to be polymerized in alphabetical order. A different aspect of polymerization is encountered in the chapter on the petroleum industry, where it causes the degradation of valuable products, such as gasoline and lubricating oils.

The chapter on polymerization in the rubber industry, 23 pages in length, is divided into three sections: natural rubber, synthetic rubber, and commercial synthetic rubber. The section on natural rubber reviews somewhat briefly research investigations, relating to polymerization, on the structure and cyclization of rubber, and vulcanization. The second section contains a general discussion of raw materials and polymerization methods used in the production of synthetic rubber. The commercial synthetics discussed are methyl rubber, butadiene rubber, chloroprene rubber, mixed polymers, and rubber-like plastics. At the end of each chapter are numerous references to the literature. Besides the regular subject index, the book has an author index. [*India Rubber World.*]

The Retardation of Chemical Reactions. By Kenneth C. Bailey. Published by Edward Arnold & Co., London, England. Available from Longmans, Green & Co., New York City. 6 × 9 in. 480 pp. \$8.00.

Although particular instances or groups of retarded reactions have been treated fully in many works on chemical kinetics, this is the first book dealing with retarda-

tions in general to appear in any language. The author, in his preface, points out the importance of understanding not only the promotion of desirable reactions, but also the retardation of undesirable ones. Each important branch of the subject is treated historically so as to reveal the gradual development of ideas, while the order of the chapters has been decided by types of reactions. The book contains 31 chapters, in addition to author and subject indices and an extensive bibliography, including a 10-page chapter on the protection of rubber. [*The Rubber Age* of New York.]

Chlorkautschuk und die ubrigen Halogenverbindungen des Kautschuks. Andreas Nielsen. Published by S. Hirzel, Leipzig, Germany, 1937. Paper, $6 \times 8\frac{3}{4}$ inches, 123 pages.

For almost ten years Dr. Nielsen has been working on chlorinated rubber and other halogen derivatives of rubber, and the present book gives the results of his experiences in this field, both in the laboratory and in the first large-scale factory for chlorinated rubber established in Tornesch. After briefly touching on rubber as a raw material, the earlier experiments with halogen and the chemical structure of rubber, the author goes into details of the production, properties, and uses of chlorinated rubber. About thirty ways in which chlorinated rubber can be used in the manufacture of both oil-free and oil varnishes and finishes are mentioned, besides its employment in the manufacture of such varied products as threads, films, artificial leather, insulation material, proofed fabrics, adhesives, floor covering, safety glass, road-building material, etc. A review of the industrial development in Germany and America as well as of the cost of production and prices concludes this section.

The succeeding chapters are devoted to a summary of the production, properties, and uses of halogen derivatives such as rubber hydrochloride, brominated rubber, iodized rubber, fluorinated rubber, etc. The author states that the most important of these, rubber hydrochloride, presents some similarities to, but also several characteristics different from chlorinated rubber. It appears to yield stronger films, but its stability can be rendered equal to that of the latter, and the cost of production is stated to be lower. The book closes with useful indices and a list of German and other patents. [*India Rubber World*.]

The Rubber Research Institute of Malaya. Published by the Institute, Kuala Lumpur, F. M. S. $6\frac{1}{2} \times 9\frac{1}{2}$ in. 20 pp.

This booklet gives the reasons for the formation of the R. R. I. M. in 1925 and its growth since that date. The function and accomplishments of its Botanical, Chemical, Pathological, and Soil Divisions are explained briefly. A description of the Experiment Station is also given. [*The Rubber Age* of New York.]

Annual Report, 1936. The Rubber Research Institute of Malaya, Kuala Lumpur, F. M. S. 158 pages.

This annual report, which covers the activities of the R. R. I. of Malaya during the year 1936, includes reports from the following divisions: soils, botanical, pathological, chemical, and experiment station. The fire which destroyed the chemical laboratory and a large amount of unpublished research data hampered the work of the chemical division considerably during 1936. Research data on the following subjects are contained in the chemical report: latex components, latex preservation, latex concentration, copper in latex, modified rubbers, clone rubber, and the drying of rubber. [*India Rubber World*.]

Recent Developments in the Rubber Industry. R. Thiollot. Gauthier-Villars, Paris, 1937. 26 pp.

In the series of monographs on the chemical industry, Thiollot has just published a booklet which sums up recent developments in the rubber industry and completes the information published in the same series and on the same subject in 1934.

This study is divided into 8 chapters, which deal with the production of the raw material, accessory products for the rubber industry, coloring ingredients for rubber, fillers, the manufacture of rubber products, artificial rubbers, products derived from rubber, and various problems connected with reclaimed rubber, factice, fireproof rubber, etc.

Each chapter includes a summary of the most important developments during the last few years, as well as a condensed summary of representative publications dealing with the subjects covered in each chapter.

At the end of the work there are also a bibliography and a table of substances. [*La Revue générale du caoutchouc.*]

Thorpe's Dictionary of Applied Chemistry. Fourth edition, Vol. I, A-Bi. By Jocelyn Field Thorpe and M. A. Whiteley, Assisted by Eminent Contributors. Longmans, Green and Company, 114 Fifth Avenue, New York, N. Y., 1936. xxvii + 703 pp. Illustrated. 23.5 × 16 cm. Price \$25.00.

All chemists who are familiar with the earlier edition of this standard reference work will realize that the name "Dictionary" does not do full justice to the scope and thoroughness of the information supplied. Although the great majority of entries are treated in a few lines in a dictionary style, there are many longer articles which give an encyclopediac character to the volumes. Thus, for example, this first volume contains long detailed articles on acetic acid, acetylenes, acridine, adsorption, alcohol, alizarin and allied dyestuffs, aluminum, amino acids, ammonia, apples, arsenic, arsenical drugs, autoclaves, balances, barbituric acid, barium, barley, benzene, bile pigments, bismuth, and many others.

In their foreword the editors make the following announcement: "The new edition of the Dictionary has been planned so as to embody the monographical aspect present in the supplementary volumes as well as the Dictionary style of the previous edition. It is intended to publish one volume yearly, the last volume containing a General Index and Glossary. The publication of the work over a prolonged period means that a slightly modified system has to be introduced to avoid giving in the earlier volumes reference to volumes which may not appear for some years. To ensure this, each volume will be used as a means of bringing a previous volume up to date. Thus each item of importance contained in a general article in an earlier volume will be dealt with in a later volume under its own initial letter, and any up-to-date additions included. In a similar manner earlier volumes will contain items of importance dealt with in general articles in later volumes, and in this case such items will be brought up to date in the later volume."

The third edition required 601 pages to cover the same part of the alphabet as the 703 pages of the first volume of the fourth edition. A detailed comparison of portions of the fourth and third editions shows, however, that the new matter added is in much greater ratio than this because much has been omitted from the old edition and there has been much revision in details.

The type is eight point solid, which at least for the reviewer's eyes is uncomfortably small for continuous reading. This new edition of Thorpe's Dictionary obviously belongs in all chemical reference libraries and will be much used. It is

especially useful as a source of information of the real chemical composition of articles sold under trade names. [*Journal of the American Chemical Society.*]

Hackh's Chemical Dictionary. Second Edition. By Ingo W. D. Hackh, with the collaboration of Julius Grant, P. Blakiston's Son and Company, Inc., 1012 Walnut Street, Philadelphia, Pennsylvania, 1937. ix + 1020 pp. Illustrated. 17.5 × 25.5 cm. Price \$12.00.

This new edition is larger by 230 pages than the first edition, published in 1929. The increase in size is due partly to the inclusion of many new terms and partly to corrections and insertions of older terms omitted from the first edition. The definitions are brief and elaborate or encyclopedic discussions are avoided, making the volume of value chiefly in reading. The style and format of the first edition are closely duplicated in the second.

It would be very easy for the reviewer of so compendious a work to become hypercritical if he should forget the extraordinary difficulties encountered in making such a compilation and the necessities imposed by limitations of space, so it should be understood at once that much praise is due Professor Hackh for the production of a monumental work of such general excellence. Nevertheless, the need for even greater completeness, and for still further broadening of the fields included, again must be urged. It is usually the word of unknown meaning, the definition and uses of which are sought by a reader, rather than the commoner terms of the scientific idiom, for he is familiar enough with these. One wonders, therefore, why many more of the rarer terms should not also be included, in order that a book which is already so valuable might be made of still greater help to the reader of scientific literature. For example, in one very limited section, under lu-, the following terms are not among those found: Ludenscheidt's alloy, ludigol, Ludlum alloy, Ludwig's reagents, Luer syringe, luigite, lumachelle, lumbofebrin, lumen alloy, Lumière's process, lyo-luminescence, lunarine, lüneburgite, lupamaric acid, lupeol, lupeone, lupylene, etc.

Some of the definitions still show a tendency to be inaccurate or incomplete. Thus, that for molecule: "The chemical combination of two or more like or unlike atoms;" for process: "Any method used in the manufacture or treatment of substances;" for monel: "a native alloy. . .;" for lyophobic: "Repelling liquids. . ." could be improved; and tetrahydro, which is an adjectival prefix, is defined as "a compound that contains. . ." etc.

The spellings and usages of the American Chemical Society are in general followed as indeed they should be.

Many names of well-known chemists are included, some of whom are now living. But if names of living chemists are to be given, it seems that some more obvious criterion of worth should be employed than is apparent, such as, in part at least, the number of references found in the name indexes of *Chemical Abstracts*. Similarly, the basis for selection of the less common trade names is not easily understood.

As stated above, it is easy to be meticulous and overcritical in commenting on a volume of this nature. Its value, however, to the reader of scientific literature related to chemistry definitely cannot possibly be overestimated. It is in the class of the most necessary and useful scientific literature, and should be as much a part of every library, public or private, as any other essential material. [*Journal of the American Chemical Society.*]

Organic Chemistry. By Frank C. Whitmore, Research Professor of Organic Chemistry, The Pennsylvania State College. D. Van Nostrand Company,

Inc., 250 Fourth Avenue, New York, N. Y., 1937. x + 1080 pp. 14.5 × 22.5 cm. Price \$7.50.

The author states definitely in the preface of his book his plan and purpose in writing an advanced text on organic chemistry. "The purpose and scope of this work can best be indicated by characterizing it as a one-volume 'Beilstein' designed for practising organic chemists, for others who have to take occasional cognizance of organic compounds and their reactions, and for students who have pursued organic chemistry for at least a year with the aid of the many excellent elementary and intermediate text-books now available."

In the opinion of the reviewer the work has been done well, and excellent judgment has been used in the selection and treatment of the substances described. Since the book is for advanced students, the author did not have to consider the pedagogical aspect of his presentation of the subject; he could accordingly compress the material and gain space for the consideration of many compounds not described in text-books of the usual type. Among the admirable features of the book are the following: a critical examination of the methods for the preparation of the more important compounds, which leads to the indication of the best method to be used in the laboratory; the description of many compounds of biochemical interest; the attention paid to newer products of the organic chemical industry; the use of the electronic concept of valence whenever this view is helpful in interpreting chemical behavior; and the fact that many of the more recent contributions to the literature are included.

The value of the book for reference is greatly increased by the fact that an unusually detailed index has been prepared, which covers 122 pages. The uses of typical synthetic methods are fully indexed. For example, the references to the Grignard reaction cover two pages; there are about 150 references to reactions of addition, 75 to conjugated systems, 40 to the Friedel-Crafts reaction, etc.

The author states in the introduction—"Instead of giving full references in the text or in footnotes the names of investigators are included in parentheses. These can be used as clues to further details in conjunction with the ordinary indexes of the chemical literature."

The number of pages allotted to the several divisions of the subject are as follows: aliphatic compounds 614, alicyclic compounds 76, aromatic compounds 183, and heterocyclic compounds 82.

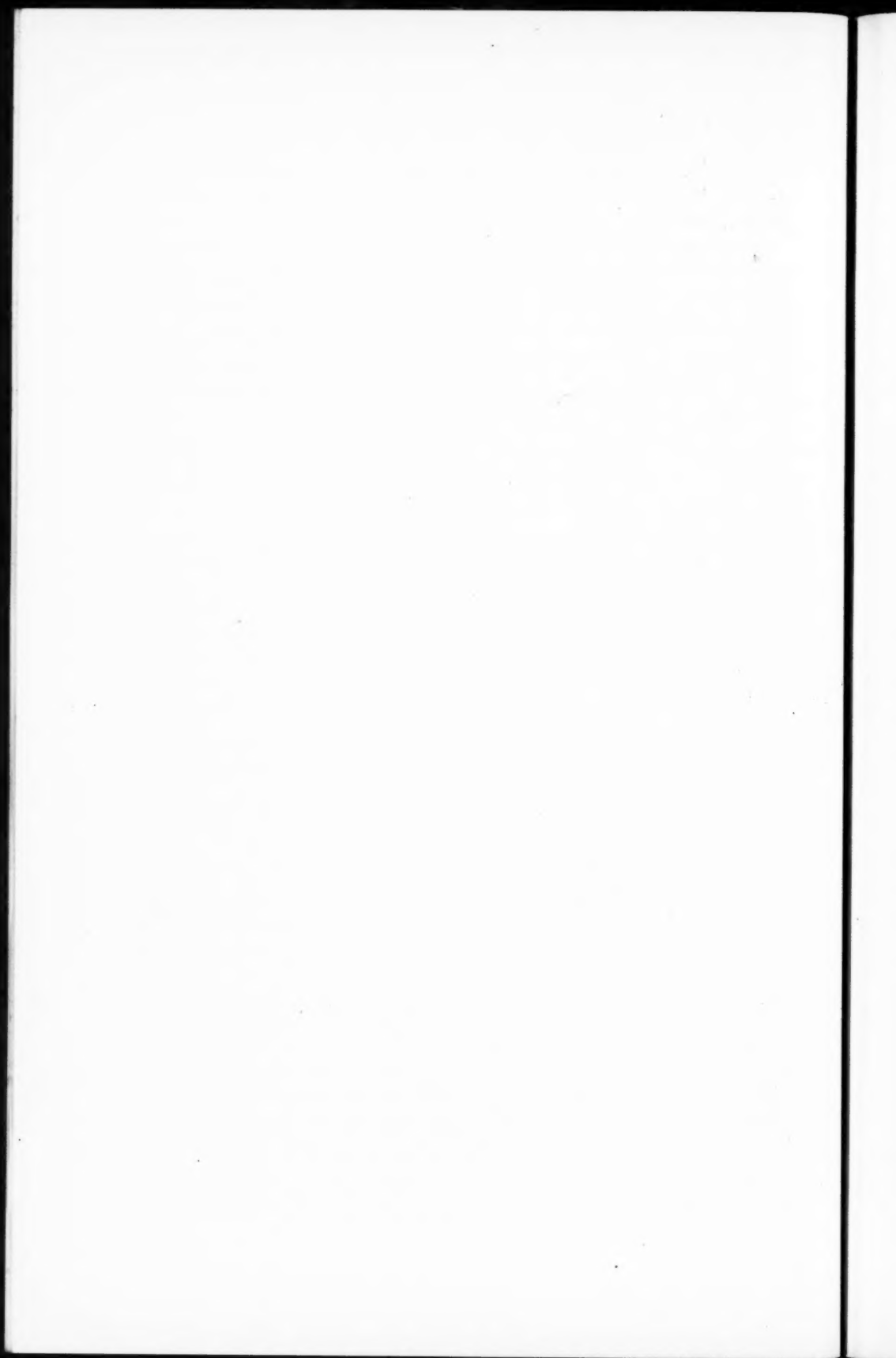
The book will be of value to advanced students who desire to broaden their knowledge of compounds and to learn more of the wide applications of the general synthetic methods used in organic chemistry. [*Journal of the American Chemical Society.*]

Chemical Engineering Catalog. Twenty-second Annual Edition, 1937. Published by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. Cloth, 1034 pages. 8 × 11 inches. Illustrated. Index.

The latest edition of this standard reference work for the process industries contains information regarding the products of several hundred concerns manufacturing engineering equipment and supplies for chemical and related industries including rubber. The volume consists of the following sections: Company Index; Trade Name Index; Equipment and Supplies, Classified Index, and Manufacturers' Catalogs; Chemicals and Raw Materials, Classified Index of Industrial, Laboratory, and Reagent Chemicals, and Manufacturers' Catalogs; and Technical and Scientific Books. [*India Rubber World.*]

A. S. T. M. Standards on Textile Materials. Published by the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Penna. 6 × 9 in. 306 pp. \$2.00.

All of the 44 standard specifications, test methods, and definitions issued by the A. S. T. M. on textile materials are included in this 1937 edition prepared, as usual, by Committee D-13 on Textile Materials. In addition, there are included a psychometric table for relative humidity, a section comprising 43 microphotographs of common textile fibers, and a convenient yarn number conversion table. A proposed method of correction of breaking strength to standard regain is also given. For the first time, new standards covering wool tops, wool felt, wool and part wool fabrics, and volumetric determination of copper are included. [*The Rubber Age* of New York.]



A Contribution to the Early History of India-Rubber

François Fresneau (1703-1770)

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In the fall of 1936 the *Revue Générale du Caoutchouc* published a special issue¹ dedicated to the memory of the French scientist La Condamine on the occasion of the bicentenary of the discovery of rubber. Quite recently the same periodical issued another special number on the occasion of the International Exposition in Paris, 1937. The title page reproduces Cochin's well-known portrait of Charles Marie de la Condamine. The first paper by Ch. Jung, entitled "History and Development of the Rubber Industry," gives all the credit of the discovery of rubber to Condamine, and for the details refers to the publication mentioned above.² In the bicentennial number, *Henri de la Condamine* gives a detailed biography of his ancestor, wherein the name of Fresneau as a correspondent of Condamine is mentioned in a few places. A second paper, by Auguste Chevalier, deals chronologically with the various publications presented by Condamine, and here Fresneau receives as much credit as can be justified from the contents of these papers. Finally, we owe a revival of the correspondence between Fresneau-Condamine and the French Minister of Colonies Bertin to J. Ch. Bongrand.³ However, when one considers the exceedingly courteous phrases and carefully couched terms characteristic of letters of that period, and bears in mind that this correspondence only refers to the last years of Fresneau's life, such documents alone cannot be taken by the historian at their full value.

A careful search of the pertinent literature, therefore, seemed essential if the part played by Fresneau in the discovery of rubber was to be clarified. Recently I succeeded in discovering a biography of Fresneau,⁴ and the following lines are intended to review briefly passages which I consider indispensable in forming an unbiased picture of his contribution to the discovery of rubber.

François Fresneau was born on September 29, 1703, in Marennes. When he was 23 years old he came to Paris to study mathematics and construction design under Professor Dupin-Duplessis. Two years later he passed his final examinations with honors, as engineer of military fortifications, and was promised a Government position at an early date. Years went by, yet nothing happened to fulfil the promise, until, through the intervention of his parents, the assistance of Mme. Henriette Antoinette de Mesmes, Marquise d'Ambres, a very influential woman in Government circles, was procured, and with her protection he obtained the certificate of royal engineer in Cayenne on August 19, 1732, with the special mission of studying the construction of new fortifications. For many years thereafter he remained the protégé of the Marquise d'Ambres. But political intrigues and professional jealousy made the life of the young and enterprising engineer difficult and often unpleasant. Nevertheless he accomplished his task satisfactorily, and was awarded several decorations and promotions.

One of the interesting episodes of his approximately fourteen years of service in Cayenne was his successful attempt to destroy the enormous hordes of ants that

seriously endangered the cultures of cocoa, coffee, and other plants. Fresneau constructed a spray gun, using sulfur as insecticide. To my knowledge, this is one of the first practical experiments made in the field of insecticides on a large scale.

After his short return to France in 1739, where he had been called to discuss his latest plans for the fortifications,⁵ Fresneau spent another period of nine years in Cayenne. These were the worst in his experience, and were partly due to increasing difficulties and intrigues in Government circles of the colony, partly also to constant warfare with pirates. Twice he handed in his resignation, but each time he was refused. In reply to the Minister of Colonies, Fresneau pointed out that the enemy had not attacked Cayenne and would not dare to in the future—a fact for which he took considerable credit. In that letter he lists practically all his contributions to his country during his stay in Cayenne, and among these we find the reference to the discovery of the rubber tree or syringe tree.⁶ His retirement was finally granted, and when he disembarked in France during the early months of 1748 he was officially decorated with the Cross of St. Louis and a substantial pension was likewise conferred upon him. He retired at his castle of La Gataudière, where he at once began a detailed report to the Minister of Colonies concerning the milk of a tree and methods of manufacturing different objects therefrom, to which he had already referred in the letter to the Minister M. Maurepas on February 19, 1746.⁷ In this letter he discusses for the first time, in writing, the discovery of a tree yielding a milk sap, from which the natives produced syringes and other useful and curious articles. The letter was accompanied by a pair of shoes made out of the milk sap by Fresneau.

Immediately upon hearing of such a tree and seeing its products, Fresneau conceived the industrial as well as commercial importance of the latter. He tried all available milk saps he could detect in the jungles about Cayenne, but with no success. At last he met some natives who had come from other districts, and, showing them some of the rubber articles, learned from them that they knew the tree from which the milk was taken. Upon his request, the natives made clay models of the fruits of the tree, molding a triangular fruit, which must contain three seeds. He also had them draw the shape of the leaves of the tree. Some time later he was given permission to travel by canoe to Aprouague, and there on both banks of the Mataruni River he found an abundance of such trees. He tapped several of them, and although, due to a long period of drought, the milk sap was slow in flowing and viscous, Fresneau was able to produce a pair of shoes and several small objects, such as syringes, bracelets, elastic balls, etc. In his detailed report Fresneau gives a description of the tree, the method of extracting the milk sap, and how to employ it. He likewise observed the rapidity with which the sap, once in contact with air, coagulates and solidifies, and that he could not redissolve it any more in that condition. He set out to find a solvent, and after many experiments, he considered nut oil (*huile de noix*) a satisfactory one.

This report, addressed to M. Rouillé, bears the date of June 17, 1749, and contains the request to forward it after perusal to the Academy of Science. It was there that the paper was handed over to Charles Marie de la Condamine for reviewing purposes.

In July, 1743, La Condamine had mentioned in his "Condensed Report on a Voyage into the Interior of Central America,"⁸ a resin called "cahuchu," found in the province of Quito. He also notes a variety of uses to which this resin was put by the natives. Being chiefly engaged in geographical and astronomical problems, La Condamine considered this matter solely as a curiosity, and did not attach any further significance to the product, of which he had dispatched a few unshaped

samples in 1736 to M. du Fay, Director of the Royal Gardens in Paris. However, when La Condamine received Fresneau's report from M. Rouillé (in 1749) and read the detailed description of how to obtain the milk sap, how to produce a variety of objects therefrom, and how to dissolve the dried resin, he decided to present this paper at a meeting of the Academy. He did this on February 26, 1751, introducing his presentation entitled "Report on an elastic resin, recently discovered at Cayenne by M. Fresneau, and on the uses of different milk saps in Guyana or Equinoctial France," with a Reprint of his diary notations of June 24, 1736, which had been hitherto unpublished. This short note carried the title "About an elastic resin called 'caoutchouc.'"⁹

La Condamine made the personal acquaintance of Fresneau in 1743 when he reached Cayenne, but we do not know whether at that time Fresneau was already aware of the existence of the rubber tree and the applicability of the milk sap, or if La Condamine first mentioned its existence to Fresneau. Whichever may have been, La Condamine makes the following and, to us, historically important introductory remark to Fresneau's report: "Since I have never given any details about the tree which produces rubber, nor about the preparation of its resin, I awaited further instructions from Para, when I received a report which left nothing further to desire on the subject. It is from M. Fresneau, Chevalier of the Military Order of St. Louis, former engineer of Cayenne, where he lived fourteen years. After prolonged search he finally discovered in this colony the tree from which the caoutchouc distills; he carefully informed himself from the Indians of Para as to the manner of procedure. Thereafter he performed himself, with the intelligence of which he has given many other proofs, a series of experiments, which were crowned with most happy success."

After the treaty of Paris, dated February 10, 1763, M. Bertin was put in charge of the Ministry of Commerce. This man had taken special interest in Condamine's Academy report, and addressed himself directly to Fresneau to obtain more detailed information as to commercial possibilities pertaining to an exploitation of rubber. A prolonged correspondence between Bertin, Fresneau, and Condamine resulted, to which reference has already been made.¹⁰ The correspondence is to be considered as one of the most interesting in the early developments of the rubber industry, and it reveals once again the prophetic eye of the practical-minded Fresneau. It is indeed amazing to see how many of Fresneau's ideas as to the advantageous use of rubber have been realized. On June 25, 1770, Fresneau died.

These are the facts which it is hoped will materially assist in clarifying the actual contributions to the discovery of rubber by these two great Frenchmen. Undoubtedly Condamine was the first to report casually the existence of a substance which today has become the basic raw material of one of the world's largest industries. But had it not been for the practical-minded engineer of Cayenne, François Fresneau, who stubbornly pursued the search for the origin of this material, and to whom we owe the first detailed description of how to obtain and apply it, Condamine's remarks would have remained buried in the archives of the French Academy until another at a later date would have rediscovered the elastic resin. With all due credit to the great scientist, La Condamine, it is apparently François Fresneau who deserves more than anyone else to be called the father of our Industry, and it is high time his name receives the place of honor which it rightly deserves.

References

¹ *Rev. Gén. Caoutchouc*, 13, No. 125 (October, 1936).

² After referring specifically to La Condamine and his discovery, Mr. Jung continues: "Other French scientists interested themselves from then on in the study of rubber; we mention especially François Fresneau, who accompanied La Condamine on one of his American excursions. . . ."

³ *Rev. Gén. Caoutchouc*, 1, 3, 43; 4, 42; 5, 34; 6, 48; 7, 43 (1924).

⁴ Baron de la Morinerie, "Les Origines du Caoutchouc, François Fresneau, Ingénieur du Roi," published in La Rochelle by Imprimerie Nouvelle Noel Texier, 1893.

⁵ He had returned to France once before in 1737, and it was on this vacation that he was married.

⁶ The translated title of the report attached to the letter, written as a reply to his unaccepted resignation, reads as follows: "... Memoirs of the services of Monsieur Fresneau, Chevalier of the Military Order of St. Louis, Captain in the Infantry, Chief Engineer at Cayenne in America, and about discoveries of greater importance as well for the services of the King and as for the colony. . . ."

⁷ Maurepas was replaced a few months later by Mr. Rouillé, who became Minister of Colonies.

⁸ Published in the proceedings of the meeting of the Academy, April 28, 1745.

⁹ These two reports were only published in 1755 in "L'Histoire et les Mémoires de l'Académie des Sciences pour l'année," 1751.

¹⁰ J. Bongrand, *loc. cit.*

Natural and Synthetic Rubber

XVIII. The Protein from Natural Rubber and Its Amino Acid Constituents

Thomas Midgley, Jr., Albert L. Henne, and Mary W. Renoll

The material remaining after the extraction of natural rubber with organic solvents has been known to contain nitrogen, and to exhibit some protein characteristics.^{1,2} The numerous communications on the subject have been compiled and sifted adequately.³ Only one investigation has been concerned with the amino acids resulting from the hydrolysis of the protein material.⁴

The purpose of the present work was to isolate a product which would be as nearly pure natural rubber protein as possible, to analyze it, and to separate and identify the individual amino acids resulting from its hydrolysis.

The starting material was the nitrogen containing residue obtained in the preparation of pure rubber hydrocarbon by fractional precipitation from a mixture of benzene and alcohol.⁵ This was a tough brown mass, entirely free of resins, but still containing a large amount of rubber, all the mineral impurities, some sugars, and the protein. Depending upon the extent of its treatment, it titrated from 3.5 to 4.2% nitrogen. This material was allowed to swell in a large quantity of xylene kept at 100° in a water-bath and never stirred. Every twenty-four hours, the liquid was decanted with the least possible stirring, and fresh or recovered xylene poured on the rubber to take its place. After a few days, the material became quite crumbly and progressively lost its tackiness. After a week xylene did not remove any more rubber. The material was then boiled with xylene to extract the last traces of rubber. The crude protein separated easily from the xylene. When boiling or stirring was resorted to too early, the protein dispersed in the rubber solution, and considerable loss occurred during decantation; moreover, separation was rendered quite incomplete and difficult to handle.

After removal of the xylene by means of boiling benzene, the protein was placed in an evaporating dish to dry in a current of air; the dry material was a friable, fluffy, tan powder, whose nitrogen content varied from 5 to 8%, and ash content from 15 to 35%. The next step consisted in electrodialyzing at 120 volts through cellophane; this removed the inorganic impurities and carbohydrates.

The purified protein, dried in a vacuum oven at 70° for six hours was a brown, crumbly mass; it amounted to about 45% of the material undergoing electrodialysis. It was analyzed for carbon and hydrogen by combustion, and for nitrogen by Kjeldahl, the final result being on an ash-free, dry basis: 57.68% C, 7.54% H, 12.52% N, and 22.28% O (computed by difference), corresponding to an empirical formula: $C_{5.35}H_{3.36}N_{1.0}O_{1.55}$, or an approximate $(C_{10}H_{16}N_2O_3)_2$.

This value for nitrogen is confirmed by the analysis of several purified samples from which prolonged extraction failed to remove any more rubber. These, when corrected for ash content, gave by titration 12% of nitrogen. A critical examination of the work of previous investigators also indicates 12% as their best value for nitrogen. These observations are stressed because of the still prevalent practice, particularly in stating the results of the analysis of rubber, of multiplying the nitrogen content by 6.25 to compute the protein content of the material, which of course arbitrarily assumes the nitrogen content of a protein to be 16%.

Hydrolysis of the purified protein material was obtained by treating 11 g. of it with 100 cc. of dilute sulfuric acid (40 cc. of concd. acid to 140 cc. of water), boiling under reflux. The hydrolyzate was filtered to remove 3.18 g. of humin, whose nitrogen content was found to be 0.7%. This humin was treated with benzene, which removed about one-half of it. From the benzene solution, alcohol precipitated a substance which had all the appearances of rubber. Making the assumption that this material was rubber, it is possible to recompute the analysis result of the protein and to find that the nitrogen content would be somewhere between 15 and 16%, which is the nitrogen content generally expected in a protein. It should, however, be repeated that removal of the last rubber by solvents was found impossible before completion of the hydrolysis.

The hydrolyzate was separated into its constituents by the carbamate method, as more recently improved.⁷ The dibasic amino acids were isolated and separated by the method of Block.⁸

When needed, final identification was obtained by preparing crystalline derivatives, according to the procedure of Crosby and Kirk⁹ and comparing them with the published photomicrographs. The picrates were used to characterize glycine, leucine, and proline, and the flavianate to identify aspartic acid and leucine.

The amino acids found and definitely identified were: glycine, aspartic acid, leucine, proline, arginine, histidine, lysine and representative of the group comprising alanine, phenylalanine, hydroxyproline, and serine. This group was not investigated further. The amino acids which were definitely absent included cystine, tyrosine, and glutamic acid.

Summary

The protein constituent of rubber has been extracted from the natural rubber by removal of the rubber hydrocarbon with solvents followed by electrodialysis of the residue. This material has been analyzed, subjected to hydrolysis, and its amino acid constituents have been separated and identified.

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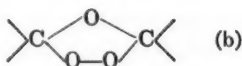
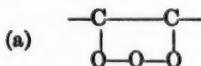
Rubber

XVIII. Various Ozonides of Rubber and the Problem of the Existence of the Primary Ozonides of Harries¹

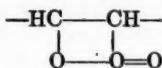
Rudolf Pummerer and Hermann Richtzenhain

I. THE QUESTION OF THE EXISTENCE OF THE OZONIDES OF THE HARRIES FORMULA

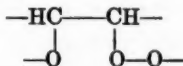
A permanently valuable service was rendered by Harries when he introduced the ozone cleavage of unsaturated compounds as a general method of investigation in organic chemistry. By analogy with other addition reactions of double bonded carbon atoms he derived the formula (a) for the ozonides which are first formed, but to support the existence of which he was able to obtain only scant experimental data. Harries relied above all on two observations, first, that mesityl oxide ozonide reverts to mesityl oxide when heated by itself,² and, secondly, that fumaric acid is supposed to combine loosely with ozone and then readily split off again.³ Both of these suppositions have remained undisputed up to the present time.



Harries reported that it was not possible, with any of a wide variety of reducing agents, to reduce the ozonides to the original compounds³ or to 1,2-glycols, as would be expected from their structure. Staudinger⁴ has laid great stress on this fundamental objection, and he considers that most ozonides have an isoözinide formula, as shown by formula (b) above, in which the carbon chain is already ruptured, so that by reduction only the usual types of cleavage products rather than glycols with intact carbon chains can be formed, as has been found experimentally. Staudinger assumed that the primary reaction products of treatment with ozone are molozonides containing the group:



which can be stabilized either by conversion into isoözonides or by polymerization to higher molecular forms.⁵ According to Staudinger, the final products should contain O and O—O groups as members of chains or rings:



Polymerization of the monomeric isoözonides formed is of no concern here, because they are extremely stable, and therefore it must be another primary product which undergoes polymerization. The constitution of monomeric butylene isoözonide was proved by Rieche and Meister synthetically by withdrawal of water from 1,2-dihydroxydiethyl peroxide.⁶

The present author has, in collaboration with Georg Matthäus, observed that when chloroform solutions of rubber and of gutta-percha are treated with ozone the

consumption of bromine by these hydrocarbons does not diminish in proportion to the ozone which is absorbed. Instead it remains unchanged almost to the termination of the ozonization, in spite of the fact that gradually increasing substitution follows the initial addition of bromine. It was attempted to explain this phenomenon on the assumption that stable molozonides or primary ozonides of the constitution proposed by Harries are perhaps formed,⁷ and that, in contrast to the rubber isoözonide formed as end product and stable towards bromide, these stable molozonides or primary ozonides can be substituted extremely readily.

These observations have led the present authors to investigate the whole subject more thoroughly, and to see whether the results of Harries, which in two cases favor his ozonide formula, could be verified.

1. The Ozonide of Mesityl Oxide

(a) *Heating Experiment.*—The ozonide was prepared according to the directions of Harries, and was heated in an attempt to bring about cleavage and thus to recover mesityl oxide. In four experiments with the ozonide, the latter exploded or deflagrated in two cases at 17° and 27° C., in other words after removal from the cold mixture but before actually heating them at all. In the other two experiments there was a slight evolution of gas at the beginning, after which the products were heated with reflux to 115° C. before they decomposed. However, contrary to the experiments of Harries and Türk,² vacuum distillation of the decomposition products gave no mesityl oxide fraction, and it could not be detected even by 2,4-dinitrophenylhydrazine. Only a series of cleavage fragments, comprising acetone (and acetone peroxide), methylglyoxal, acetic acid, and formic acid were identified.

(b) *The Reduction of Mesityl Oxide Ozonide.*—If mesityl oxide ozonide has the constitution ascribed to it by Harries, its reduction should lead unquestionably to the glycol, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{OH})\text{COCH}_3$, which was prepared by Harries and Pappos⁸ by another method. To prove this in a more certain way, a method for its detection was developed. Although Harries and Pappos stated that by reaction with *p*-bromophenylhydrazine this glycol undergoes cleavage with formation of acetone-bromophenylhydrazone or methylglyoxalbromophenylloxazone, the present authors succeeded in obtaining a very good yield, in cold 17 per cent sulfuric acid with 2,4-dinitrophenylhydrazine, of a normal dinitrophenylhydrazone, which is adapted to the detection even of very small amounts of the glycol.

However, in none of the reduction experiments was it possible, even with the mildest reducing agents such as cold hydroquinone, hydrazobenzene, aluminum amalgam, and zinc dust plus silver nitrate, to detect the presence of the glycol. Fischer, Düll, and Ertel¹¹ succeeded in splitting the ozonide by catalytic hydrogenation at very low temperatures, but they too obtained only normal cleavage products.⁹

Since it is possible that the primary ozonide is transformed very rapidly into the isoözonide, it was considered necessary to employ an apparatus in which continuous reduction could be carried out immediately after the quickest possible ozonization, in a cooled Raschig column of small size.¹⁰ With this apparatus, the results were the same as before.

2. Ozonization of Fumaric Acid and of Its Diethyl Ester

In describing the ozonization of fumaric acid, Harries³ says that it combines with ozone, but that on standing at room temperature the product gives up its

ozone, so that it is impossible to prepare the ozonide of this acid. This fact appears to lend support to the formula of ozonides proposed by Harries. The present authors are able to confirm the fact that no ozonide of fumaric acid can be obtained. According to our view, however, the reason for this failure is the extraordinary inertness of fumaric acid towards ozone. As a matter of fact, fumaric acid also combines with bromine very slowly. Experiments have led us to the conviction that, even with a large excess of fumaric acid, ozone dissolved in acetic acid remains unconsumed after 1 hour at -70°C . The fumaric acid "recovered" from the ozonide by Harries may therefore be regarded as fumaric acid which has never been attacked, so that the experiment loses its significance as evidence in the problem.

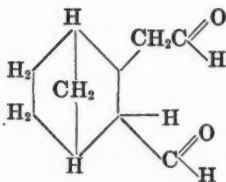
On the contrary it was found possible to prepare the hitherto unknown crystalline *diethyl ester of fumaric acid*, with melting point of $42-43^{\circ}\text{C}$., by cooling well in carbon tetrachloride. From 20 to 30 per cent excess of reagent is necessary for complete ozonization. The ester was not formed again by storage of the ozonide, but as in the case of cleavage with water, the expected ester of glyoxylic acid. Furthermore, quick reduction with aluminum amalgam of the ozonide prepared in ethyl acetate at -55°C . gave no indication whatsoever of the existence of a molozonide, which would necessarily yield ethyl tartrate. In this case too the only product was the ester of glyoxylic acid.

3. Ozonization of Dihydrodicyclopentadiene

This repetition of the experiments of Harries on fumaric acid showed that no clue was to be obtained in this way as to the formation of a stable primary ozonide with the carbon chain still intact. On the other hand, Staudinger came to the conclusion that molozonides are primary reaction products, especially in the case of hydrocarbons such as cyclopentene, cyclohexene, cycloheptene, dicyclopentadiene, and dihydrodicyclopentadiene, which form both monomeric and polymeric ozonides. We have ourselves studied the ozonization of dihydrodicyclopentadiene¹¹ from the point of view of determining whether a molozonide may perhaps be formed and then be reduced to the glycol.

In carbon tetrachloride Staudinger obtained a white, powdery ozonide, which fused at $125-130^{\circ}\text{C}$., which was easily soluble in benzene, carbon tetrachloride, and carbon disulfide (though colloidal solutions were formed), and which showed molecular weights of 3840 and 6250 by the cryoscopic method. This ozonide was insoluble in ether and in petroleum ether.

In the present work, the attempt was made to avoid polymerization and any molecular rearrangement of the molozonide in ethyl acetate at -75°C . by bringing about cleavage by hydrogenation with hydrogen, with platinum-silica gel as catalyst. However, both at 0° and 20°C . there was only a slight absorption of hydrogen, a result which it would be difficult to understand of a molozonide. Then again the ozonide liberated iodine from hydrogen iodide only very slowly, and behaved differently from the ozonide described by Staudinger. When it was precipitated from its benzene solution by petroleum ether, it yielded a white powder, with melting point of $60-62^{\circ}\text{C}$., which was very easily soluble in ether. Since it did not undergo satisfactory cleavage with mild reagents, it was decomposed by zinc dust and acetic acid. Under these conditions the reaction was normal, and there was formed the hitherto unknown *3',6'-endomethylenehexahydrohomophthalaldehyde*, with boiling point 112°C . under 0.3 mm. pressure.



II. FOLLOWING THE PROGRESS OF OZONIZATION OF RUBBER AND OTHER COMPOUNDS BY TITRATION WITH BROMINE

The addition of ozone to unsaturated compounds is carried out in organic laboratories many times every day, and it is customary to regard ozonization as complete when in a quick test bromine is no longer consumed by a sample removed from the reaction mixture. Even today, however, there have been no data to show whether or not it is possible to follow the progress of saturation of double bonds *during* ozonization by titration with bromine.

We had occasion at one time to test this possibility with rubber, and very surprising results were obtained. In spite of treatment with ozone, the consumption of bromine by the rubber solution remained nearly the same almost to the end of the ozonization. There was also convincing evidence that all of the ozone reacted with the chloroform solution, since no iodine was liberated from aqueous potassium iodide afterwards. Only shortly before the reaction was ended did unconsumed ozone react with the potassium iodide. The term "critical point" is suggested for this point in the reaction because, commencing at about this moment, the consumption of bromine by the solution diminished rapidly to zero within a few minutes (see Fig. 1, curve *a*).

Later an observation of Matthäus and one of the present authors made it appear as if the particular rubber ozonide which is relatively stable to bromine had been formed only by the last portion of ozone, while previous to its formation an unstable ozonide (primary ozonide) of some kind was present in solution, and this underwent some kind of a transformation by the action of excess ozone.¹² This led to our experiments with primary ozonides.

It was soon found that partially ozonized rubber behaved quite abnormally when titrated with bromine, a behavior which has been found to be also true only of gutta-percha (see Fig. 1, curve *b*). Gutta-percha (2.5 grams) was ozonized in carbon tetrachloride (80 cc.) at 0° C. with 5.5 per cent ozone. Each 5 cc. were titrated with 0.1 *N* bromine solution (until the color of the bromine in 1 drop persisted for 10 minutes). On removal of the last sample, unconsumed ozone had passed through the ozonizing chamber. The evolution of hydrogen bromide in the titration increased somewhat with the time of treatment with ozone. The normal reaction which had been expected to take place would have been a gradual, uniform decrease in consumption of bromine by the solution being ozonized in direct proportion to the absorption of ozone. A normal curve of this kind is obtained by titration during the ozonization of 2-methyl-2-butene, 3-ethyl-2-pentene, cyclohexene, and mesityl oxide (see Fig. 2).

A 2.05 per cent solution of freshly distilled amylene in carbon tetrachloride was ozonized with 1.5 per cent ozone at 15° C. At definite time intervals during the ozonization, 5 cc. units of the reaction mixture were removed with a pipette and titrated with 0.1 *N* bromine solution. Table III shows that the number of double bonds decreased uniformly with continuation of the time of treatment with ozone. In further experiments a special study was devoted to unsaturated compounds in

which there was likelihood of the existence of primary ozonides, from the point of view either of Harries or of Staudinger. The compounds chosen were mesityl oxide and cyclohexene, and the method of analysis was titration with bromine. Here too it at first appeared as if the bromine value of the reaction mixture were practically constant during the first few quarter-hour periods of ozonization,⁷ but a more careful investigation failed to confirm this earlier supposition. Furthermore, the prox-

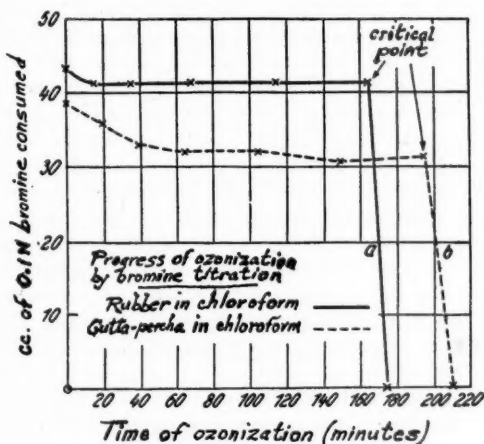


Figure 1

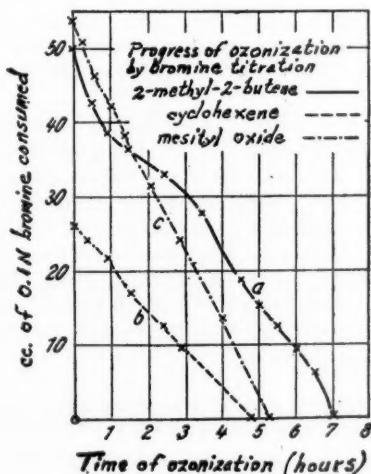


Figure 2

imity of the keto group to the ozonide group in mesityl oxide results in a behavior different from that of rubber. The accumulation of ozonide groups is a determinant factor in the behavior. Nevertheless, β -ionone, which takes up 2 molecules of ozone, behaves on titration in a quite normal manner, like mesityl oxide.¹³ Particularly convincing evidence has been obtained that synthetic monomeric butylene ozonide in carbon tetrachloride is stable towards traces of bromine for many hours.

The constancy of the bromine consumption during ozonization probably cannot be attributed to the fact that loosely combined ozone at the double bond is displaced by bromine. On the contrary, the constancy of the bromine added is only apparent, in fact Pummerer and Matthäus⁷ have found that the longer a solution is treated with ozone the greater the proportion of bromine consumed by substitution. Only the sum of the bromine consumed by addition plus that consumed by substitution remains constant as a matter of coincidence. The hydrogen bromide which is formed can be determined by the iodide-iodate method of MacIlhiney, and it can also be removed by suction from the ozonized rubber solution after titration is completed. By this latter method, which is perhaps the more reliable one in the present case, only a scanty one-third of the total bromine is obtained in the form of hydrogen bromide when the critical point is reached, in spite of the fact that one-half would be expected if only substitution were to take place. To this should be added the fact that the ozonide groups themselves consume hydrogen bromide and thus remove the latter from the sphere of action in the test. Rubber ozonide + hydrogen bromide soon decompose with appearance of a brown coloration.

We are, however, confronted with the fact that at the critical point a rubber ozonide in which bromine is very easily substituted is present in the reaction mixture, and that within a few minutes it becomes stable towards bromine. It was found to be possible to obtain the substitution product by reduction with sulfurous acid; this product turned out to be the already familiar β -bromolevulinic acid, which was isolated in 32.8 per cent theoretical yield. A small yield of β,β -dibromolevulinic acid was also obtained. Bromination therefore involved the CH_3 group on the ozonide ring and its CH_2 group, but perhaps not the CH group of the double bond. These compounds were also prepared by Harries by the action of a large excess of bromine on rubber ozonide for 18 hours, whereas with the "primary ozonide" in the present investigation they formed as rapidly as titration could be carried out. On the contrary, the final rubber ozonide is stable to traces of bromine during a ten-minute test.

It is worthy of mention that rubber can be titrated better with pyridine dibromide hydrobromide, already recommended by Rosenmund and Kuhnenn¹⁴ for other purposes, than with free bromine. Here too the consumption of bromine by the solution remains constant for 1 hour or more, in spite of continuous treatment with ozone; it then diminishes gradually before the critical point is reached. Figure 3 shows this phenomenon, and also the difference in reactivity between the dibromide and free bromine. Finally it was proved conclusively that the oxide of rubber, prepared from rubber and perbenzoic acid,¹⁵ is stable towards bromine, and that mixtures of rubber and rubber oxide in chloroform react in a normal manner until the double bonds have all been exhausted.

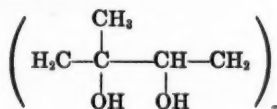
III. THE RUBBER OZONIDE WHICH REACTS WITH BROMINE AND THE RUBBER OZONIDE WHICH IS STABLE TOWARDS BROMINE

The next problem was to isolate the rubber ozonide which was present when the critical point was reached, and also the subsequent isoözonide which was stable to bromine. Both were isolated by concentration of the chloroform solution in a vacuum and final precipitation with petroleum ether. After drying in a high vacuum, both had the normal composition $(\text{C}_5\text{H}_6\text{O}_3)_n$. The bromine consumption of the "primary ozonide" varied, but it reached 91 per cent of the quantity which the fundamental rubber molecule should consume. The final ozonide was in this case, as previously, stable towards bromine. The physical and chemical properties of both preparations were hardly distinguishable; the stability of the "primary ozonide" is surprisingly great, and it can be reprecipitated repeatedly. In solution the

"primary ozonide" is even more stable, and a chloroform solution obtained at the critical point remained apparently unaltered on storage in a refrigerator for 14 days, whereas levulinic peroxide was precipitated from a solution of the final ozonide.

Pummerer, Ebermeyer, and Gerlach¹⁶ have already shown that the rubber ozonide which has been modified in this way by separation of the peroxide becomes soluble in ether. It is therefore a decomposition product and should no longer bear the name of a rubber ozonide, for ozonides of rubber are insoluble in ether.

Experiments were then carried out to determine whether the "primary ozonide" yields a polyglycol of the composition:



by cautious reduction with aluminum amalgam or zinc dust, as was attempted in the earlier work (see page 8). But in this case too the attempts were unsuccessful,

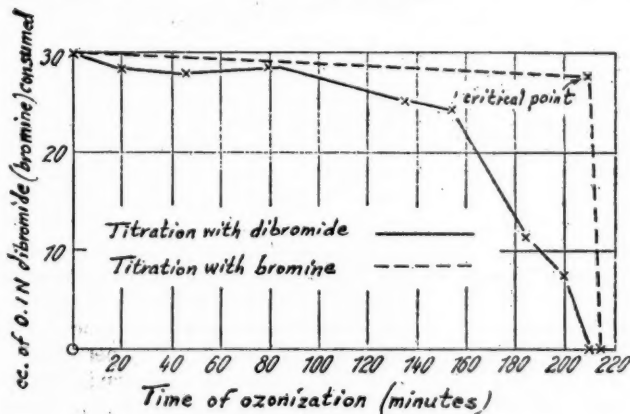


Figure 3

and only normal cleavage fragments were formed, so that the hypothesis of a "primary ozonide" really has no longer any foundation in fact. Furthermore, when the experiments described in the early part of this paper (Section I) were repeated, they likewise disproved the existence of other primary ozonides having the constitution proposed by Harries.

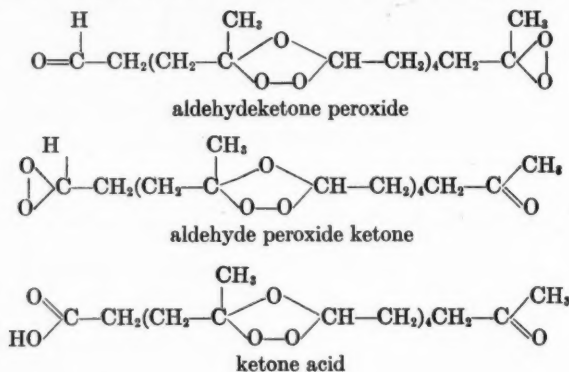
In view of these negative experimental results, it became necessary to explain in some way, other than by a transformation hypothesis, the change which the rubber ozonide undergoes beyond the critical point. Accordingly a search was made for other oxidizing agents which behave in the same way towards the "critical" ozonide as does the ozone treatment during the last few minutes. It was found that the number of useful reagents is extremely small, in fact perbenzoic acid was the only reagent found with a similar effect, while benzoyl peroxide had no effect, hydrogen peroxide only a slight effect, and halogens no effect. Consequently the assumption of a final residual, terminal (perhaps conjugated) carbon double bond, in the rubber chain, which is not attacked by ozone, is not justified.

Very long carbon chains in the two rubber ozonides are in general no longer to be considered. A molecular weight in bromoform of 580, corresponding to $(\text{C}_7\text{H}_8\text{O}_3)_n$,

was found for both ozonides, whereas in benzene Harries found somewhat lower values. The rubber chain is therefore broken down to a great extent. The softening temperature of the products was approximately 35° C., while decomposition with evolution of gas commenced, as reported by Harries, at 45° C.

A hitherto unknown, difficultly soluble, and probably higher molecular ozonide of rubber can be obtained in carbon tetrachloride. However, since this new compound leads to no new point of view in the immediate problem to be solved, it will not be discussed until later (see Section IV).

The rubber ozonide (C₅H₈O₃)₅, the analysis of which agreed strictly with a penta compound, can be formulated in three ways with various end groups:



The question of the way in which perbenzoic acid overcomes the sensitivity of the primary ozonide to bromine can be explained with the aid of comparative experiments. Other substitution reactions with bromine, such as those with acetone and ethyl acetoacetate, can be stopped by perbenzoic acid. In the case of acetone, as shown in Fig. 4, relatively small quantities of perbenzoic acid are sufficient to retard greatly substitution by bromine, while, as Fig. 5 shows, larger proportions are necessary in the case of ethyl acetoacetate. However, in both cases the quantities are of the same general order of magnitude as those of the bromine to be decolorized.

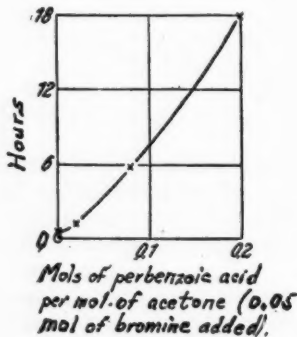


Figure 4

A strictly similar relationship is found in the case of the ozonide of rubber, as is evident in Fig. 6. It is not necessary to assume that perbenzoic acid is itself transformed in its reaction with the bromine-sensitive rubber ozonide, or

that it acts as an oxidizing agent, but merely that in some way it suppresses the bromine-substitution reaction as it does with acetone. In the stabilization of the ozonide by the last portions of ozone, the possibility of conversion of an aldehydeketone peroxide into a peracid must be considered. Oxygen alone is frequently sufficient to accomplish this (*e. g.*, in the case of benzaldehyde), and according to F. G. Fischer oxidation of aldehydes to peracids in the presence of ozone takes place very readily without all of the ozone being consumed. In this reaction molecular oxygen is activated in some way.¹⁷ During the final moments of the reaction, the

small quantity of ozone is therefore sufficient to produce enough rubber ozonide peracid for the latter to be able to stop bromine substitution to the same extent that perbenzoic acid does. Bromination of acetone can in fact be arrested by the stabilized rubber ozonide.

It is possible to explain the action of perbenzoic acid in two different ways.

(1) It removes the positive catalyst of the bromine substitution, a part which hydrogen bromide has been known to play in many bromination reactions. This possibility was discussed after the address of one of the authors before the German Rubber Society at Munich in 1936 in answer to a question by B. Rassow about the fate of perbenzoic acid,¹⁸ and meantime the results of further experiments have favored this explanation. Thus acetone decolorizes bromine immediately in the presence of hydrogen bromide, but only very slowly in its absence.¹⁹ In an inert medium, perbenzoic acid is decomposed immediately by hydrogen bromide, with separation of bromine.

(2) Perbenzoic acid may promote a chain reaction to the point of rupture,

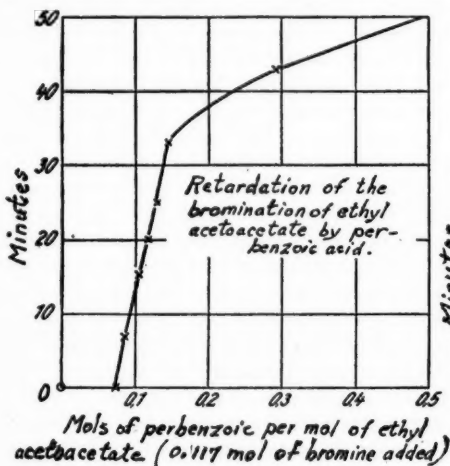


Figure 5

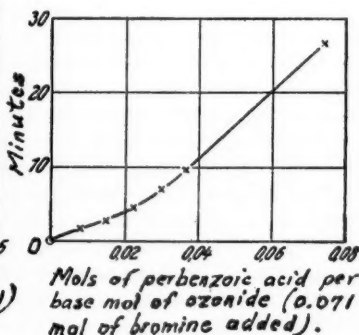


Figure 6

whereby not only bromine atoms but also free radicals with trivalent carbon as chain carrier are formed. Such a concept has already been advanced to explain both the addition of halogens and substitution by halogens in light; in fact in reactions of halogens with aliphatic compounds in light this mechanism plays a determinant part.²⁰ In the above case the first explanation (1) is more natural and satisfactory. Whether in addition to this there is the effect described in the second explanation (2) can perhaps be proved by experiments in darkness.

IV. A NEW DIFFICULTLY SOLUBLE RUBBER OZONIDE

A hitherto unknown, difficultly soluble ozonide of rubber can be prepared in carbon tetrachloride. Whereas in the case of ozonization in chloroform the rubber ozonide remains in solution, in carbon tetrachloride it precipitates very rapidly. This discovery is at variance with the information given by Harries, who suggests that rubber can be separated from rubber resins in virtue of the fact that the former is not precipitated by ozone in carbon tetrachloride.²¹ Sol rubber and crepe rubber

were found to behave in the same way in this respect. A study of the spontaneously precipitated rubber ozonide, thus prepared for the first time, led to a particularly interesting result concerning its reactivity from a kinetic point of view.

It is a reasonable assumption that the ozone which is introduced is distributed uniformly among all the molecules of rubber. Contrary to what might be expected, however, it was found that even with an excess of ozone the chief product was the final ozonide of rubber, and therefore that, once attacked, a rubber molecule has a strong tendency to react completely. Thus, if only 60 per cent of the calculated proportion of ozone is introduced into a carbon tetrachloride solution of sol rubber, an ozonide of the normal composition $(C_8H_8O_3)_n$ precipitates directly, with a yield of 67 per cent, based on the ozone introduced. At the same time, 15 per cent of almost unchanged rubber can be isolated from the solution and this rubber contains only 3 per cent of oxygen, which possibly is in ozonide form.

The rubber ozonide prepared in carbon tetrachloride is different from the ordinary ozonide prepared in chloroform by Harries. After thorough washing and elimination of solvent, the white flocculent precipitate showed a softening point of 85°C ., in contrast to 45°C . for the ozonide prepared in chloroform. Then again it was much more difficultly soluble in ordinary solvents such as chloroform, benzene, and ethyl acetate. These properties made it probable that this new ozonide had a higher molecular weight than that of the more familiar ozonide. This is in harmony with observations of Harries²² and of Staudinger,²³ both of whom found higher molecular weights for ozonides of other compounds in carbon tetrachloride. In the case of rubber, it is doubtful whether the ozonide which soon precipitates spontaneously is less degraded by decomposition and therefore contains a relatively long rubber ozonide chain, or whether it is a polymeric ozonide in which several rubber chains are united by O_2 and O bridges. The parallelism with the other experiments in carbon tetrachloride seems to favor this latter assumption. Among other properties of the new ozonide which are worthy of note is its slight reactivity towards hydrogen iodide and towards bromine. It had been expected that an ozonide which has been precipitated spontaneously with a great deficiency of ozone would show properties similar to those of the "critical" ozonide, *e. g.*, would show a high bromine consumption. This latter was, however, only about 19 per cent, a low value which is perhaps attributable to the presence of other (larger) isoözonide rings in the polymeric ozonide.

Still more surprising was the fact that, when determined cryoscopically in bromoform, the molecular weight of the difficultly soluble ozonide had exactly the same value, *viz.*, 580, corresponding to the composition $(C_8H_8O_3)_n$, as that of the regular ozonide. Evidently bromoform, as a solvent of strongly dipolar character, degrades the difficultly soluble ozonide during the molecular weight determination in the same way that chloroform as solvent does during ozonization. This phenomenon lends support to the idea that the common ozonide and the new difficultly soluble ozonide belong to the same homologous series of polymers, and differ only in the lengths of their ozonide chains.

In the investigation described in the present paper, we have made various observations, which in some cases apparently favor the relatively stable character of primary ozonides in the sense intended by Harries, but which on closer examination give no evidence of existing. In view of this, it seems unnecessary to distinguish in nomenclature between ozonides and isoözonides. Ozonides which can be isolated do not actually contain the Harries ring system (a) (see page 7), but ring system (b) (see page 7) proposed by Staudinger. The origin of polymeric ozonides, the existence of which can be proved in many cases, can be explained best,

as already mentioned, on the assumption of Staudinger⁵ that micropenices are first formed, but that these are a very unstable transitory step in the process.

EXPERIMENTAL PART

I

1. MESITYL OXIDE OZONIDE

Preparation of Pure Mesityl Oxide.—Mesityl oxide was prepared from diacetone alcohol. Since in spite of the most careful storage in nitrogen in a brown bottle this compound turned yellow rather rapidly and could not be obtained in colorless form again even by repeated vacuum distillations, it was converted into its bisulfite derivative, and this was decomposed again by means of alkali. Although Harries²⁴ found that mesityl oxide is only partially soluble in bisulfite solution, and sought to explain this behavior by the formation of a more finely divided physical isomer, we were able to prove in the present investigation that mesityl oxide actually does dissolve completely, though very slowly, in bisulfite solution. The mesityl oxide recovered from the bisulfite compound had a constant boiling point of 34° C. under 12 mm. pressure, and remained colorless when kept in nitrogen in a brown bottle for a month. Titration with a carbon tetrachloride solution of bromine gave the correct value. The point at which the color of the bromine solution added remained for 10 minutes was chosen as the end-point of the titration. This method is designated as the "ten-minute procedure" in the following pages.

Analysis

0.1424 gram of compound
0.1 N bromine solution
Value calculated: 29.04 cc.
Value found: 29.06 cc.

2,4-Dinitrophenylhydrazone of Dihydroxydihydromesityl Oxide.—A concentrated aqueous solution of dihydroxydihydromesityl oxide²⁵ was treated with a slight excess of a 1 per cent solution of 2,4-dinitrophenylhydrazine in 17 per cent sulfuric acid. A yellow precipitate formed immediately, and after 2 hours this was filtered and was recrystallized repeatedly from 40 per cent alcohol. It formed fine orange-yellow needles, with melting point 164–166° C. (decomposition). It colored a methanol solution of potassium hydroxide intense red.

Analysis

5.108 mg. of substance: 8.781 mg. CO₂; 2.425 mg. H₂O
3.442 mg. of substance: 0.556 cc. N (34° C., 739 mm.)
C₁₂H₁₀O₆N₄: Calculated: C 46.13 H 5.17 N 17.95
 Found: 46.88 5.31 18.06

Experiments on the Reduction of Mesityl Oxide Ozonide

With Aluminum Amalgam.—A solution of 5 grams of mesityl oxide in 40 cc. of ethyl acetate was ozonized at –15° C. with 8 per cent ozone until stable to bromine. Immediately after completion of the ozonization, 5 grams of aluminum amalgam were added to the solution, and following this the correct amount of water for the reaction was slowly dropped in with vigorous stirring. After the titanium reaction for hydrogen peroxide was no longer positive, the ethyl acetate solution was separated by fractional distillation. Acetone distilled with the solvent (melting point of the dinitrophenylhydrazone 127–128° C.). A small yield of formic acid was recovered.

Three more fractions were obtained at a pressure of 12 mm.

- (1) 20–24° C.
- (2) 24–45° C.
- (3) 45–50° C.

* Fraction (1) had an acid reaction (formic acid and acetic acid), and reduced ammoniacal silver solution and Fehling solution. A dinitrophenylhydrazone with melting point 179°C . probably represented a small yield of acetol or methylglyoxal.

Fractions (2) and (3) yielded the osazone of methylglyoxal, with melting point 149°C .

Apparatus for Rapid Ozonization by the Counter-Current Principle, and for Reducing Ozonides Immediately after They Are Formed²⁶

The chamber in which ozonization was carried out was a glass tube, 60 cm. long and 2 cm. in diameter, filled with small glass Rashig rings, and surrounded by a cooling jacket (see Fig. 7). At its upper end was a ground-glass bulb with dropping cock and tube attached to lead away excess oxygen. The solution to be ozonized was precooled by a refrigerating coil. The ozone was introduced through a tube bent downward at the bottom of the ozonizing tube. A round-bottom flask of 500 cc. capacity, connected with the ozonizing tube by a ground-glass connection, received the ozonized solution from a tube bent around like a siphon. Reduction was carried out in this flask with mechanical agitation. The inlet for ozone was connected with the ozone apparatus, and the outlet for the ozone with the exhaust gas collecting tube by ordinary ground-glass joints.²⁷



Figure 7

Reduction with Zinc Dust.—In the apparatus described, 8 grams of mesityl oxide in 190 cc. of ethyl acetate were ozonized at -10°C . with 5.5 per cent ozone. The mesityl oxide solution was precooled and introduced dropwise, while the rate of flow of the ozonized oxygen introduced was 3.7 liters per hour for a total time of 15 hours. The reduction flask, the contents of which were stirred from the beginning until 1 hour after completion of ozonization, contained 25 grams of zinc dust, 12 cc. of water, some silver nitrate and hydroquinone, and 50 cc. of dioxan. At the end of an experiment, the dried ethyl acetate solution was distilled, and the residue was vacuum-distilled. In this way there were obtained three fractions: (1) $24-32^{\circ}\text{C}$. (12 mm.); (2) $32-48^{\circ}\text{C}$. (chiefly at $44-48^{\circ}\text{C}$.), and (3) $70-81^{\circ}\text{C}$. (3 drops of a pale yellow liquid). Fractions (1) and (2) reduced cold Fehling solution, and with phenylhydrazine gave a large quantity of methylglyoxal osazone. Acetol, formed by reduction of methylglyoxal, was probably present and, unlike the latter, was capable of reducing Fehling solution, even in the cold.

The product recovered from fraction (3) by 2,4-dinitrophenylhydrazine fused at $265-270^{\circ}\text{C}$. and, after recrystallization from alcohol, at 305°C . It colored alcoholic alkalis violet, and may have been methylglyoxaldinitrosoazone, which fuses at 312°C .

Experiments on Heating Mesityl Oxide Ozonide

In these experiments, 10 grams of mesityl oxide without solvent were ozonized at -20°C . with 8-10 per cent ozone exactly to the point of stability to bromine. The yield of ozonide was quantitative.

In the first experiment, the ozonide, which had stood over night in a refrigerator, was warmed very slowly in a flask, provided with a reflux condenser, in an oil bath. Even at 27°C . the ozonide decomposed, with active deflagration.

In the second experiment a slight temporary evolution of gas took place shortly

after removal of the ozonide from the freezing mixture. This time the ozonide was warmed gradually to 115° C., in which case a small quantity of acetone peroxide, with melting point 130° C., collected in the reflux condenser. A yield of 12.4 grams of decomposition products was obtained from 14 grams of ozonide.

In the third experiment, which was carried out in exactly the same way, 13.7 grams of ozonide yielded 11.9 grams of decomposition products. The two products were combined and submitted to vacuum distillation. At a pressure of 14 mm. there was collected in a spiral, refrigerated with an ether-carbon dioxide mixture, 6.4 grams of acetone containing formic acid. In the first receiver, 8.2 grams of a colorless liquid consisting of a mixture of acetic acid and formic acid condensed up to 28° C. The next fraction weighing 1.1 grams, collected at 28–38° C. (12 mm. pressure), was pale yellow, and should have contained the residual mesityl oxide. The odor indicated that this might have been so, but the oxide could not be detected either by decolorization of bromine solution or with the aid of 2,4-dinitrophenylhydrazine. On further distillation up to 85° C., there passed over a yellow oil, and then a brown oil, which contained considerable quantities of methylglyoxal. These oils were not analyzed further. The residue was essentially resinous.

In a subsequent experiment the ozonide exploded violently after standing for a short time at 17° C.

Control of the Progress of Ozonization by Titration with Bromine

In these experiments, of which only two will be mentioned, samples of 5 cc. each were withdrawn after definite time intervals during ozonization of a solution of mesityl oxide in carbon tetrachloride, and were titrated with 0.1 *N* bromine solution by the ten-minute procedure. The carbon tetrachloride necessary for these analyses was dried by phosphorous pentoxide, and was then distilled.

Experiment (1).—5.51 grams of mesityl oxide were dissolved in 100 cc. of carbon tetrachloride and were ozonized at 15° C. with 8% ozone.

TABLE I (Fig. 4)

Time of ozonization (min.)	0	15	35	60	85	125	175	240	320
Volume of 0.1 <i>N</i> bromine (cc.)	53.30	50.32	46.25	42.24	38.12	31.17	24.00	13.19	0

Experiment (2).—To a solution of 4.3 grams of mesityl oxide in 100 cc. of carbon tetrachloride, which was ozonized at –15° C. with 5.5% ozone, phosphorous pentoxide also was added to exclude every trace of moisture.

TABLE II

Time of ozonization (min.)	0	15	35	50	80	110	140	160
Volume of 0.1 <i>N</i> bromine (cc.)	40.46	38.04	34.31	31.60	23.88	15.23	6.95	0

2. OZONIZATION OF FUMARIC ACID AND OF DIETHYL FUMARATE

Attempt to Prepare an Ozonide of Fumaric Acid.—Two grams of finely pulverized fumaric acid were suspended in 70 cc. of pure ethyl acetate, and 5.5% ozone was passed into the suspension at –70° C. Shortly after commencing the treatment with ozone, unconsumed ozone passed through the ozonizing tube. After passage of ozone for several hours, most of the fumaric acid remained unaltered in the bottom of the reaction mixture; the dissolved portion was recovered almost quantitatively after removal of the ethyl acetate in a vacuum.

When finely pulverized fumaric acid was added to a solution of ozone in ethyl

acetate at -70°C ., the relatively little dissolved ozone was still unconsumed after 2 hours, and was recognizable by the blue color.

Ozonide of Diethyl Fumarate.—Six grams of diethyl fumarate were ozonized in 40 cc. of carbon tetrachloride at -15°C . by 5.5% ozone. The ozone which passed into the solution was not completely absorbed. After introduction of about 120 per cent of the theoretical quantity of ozone, the ozonide, which crystallized in the form of long needles, was filtered and was washed with a liberal quantity of petroleum ether of low-boiling range. This treatment gave directly an analytically pure ozonide, with melting point of $42-43^{\circ}\text{C}$.

Analysis							
Substance:	4.640 grams	CO ₂	7.441 mg.				
		H ₂ O	2.239 mg.				
C ₈ H ₁₂ O ₇ :	Calculated:	C	43.63	Found:	C	43.74	
		H	5.50		H	5.40	

In the carbon tetrachloride solution there remained, in addition to unaltered diethyl fumarate, some ozonide which could be isolated by concentration in a vacuum.

Reduction of the Ozonide with Aluminum Amalgam.—Ozone at 5.5% concentration was passed into a solution of 8 grams of diethyl fumarate in 80 cc. of ethyl acetate at -55°C . After introduction of 130 per cent of the theoretical quantity of ozone, an excess of aluminum amalgam was added to the clear, colorless solution of the ozonide, and the water necessary for reduction was dropped in slowly with vigorous stirring. After 3.5 hours, iodine was no longer precipitated from acidified potassium iodide solution. The mixture was then filtered, and after removal by distillation of the ethyl acetate and the ethyl glyoxylate formed, which was identified by its phenylhydrazone (m. p. 228°C .), vacuum distillation yielded 1 gram of unaltered diethyl fumarate. The distillation residue, which amounted to 0.5 gram, should, if a molozonide were present, have contained ethyl tartrate. However, after saponification with sodium hydroxide solution, no tartaric acid could be detected. Likewise, no tartaric acid could be identified in the aluminum sludge.

3. OZONIZATION OF DIHYDRODICYCLOPENTADIENE

Seven grams of dihydrodicyclopentadiene were dissolved in 80 cc. of pure ethyl acetate, and ozonized with 5.5 per cent ozone. The ozone which was passed in was absorbed completely. The ozonide solution was then clear and colorless. After removal of the ethyl acetate in a high vacuum, the ozonide remained behind as a colorless, extremely viscous oil, which solidified on long standing in a freezing mixture. By trituration with cold petroleum ether, a white powdery mass was obtained, and this was purified further by solution in a little benzene and precipitation by petroleum ether. It then fused at $60-62^{\circ}\text{C}$., with evolution of considerable gas.

Analysis							
Substance:	4.369 grams:	CO ₂	10.720 mg.				
		H ₂ O	3.240 mg.				
C ₁₀ H ₁₄ O ₃ :	Calculated:	C	65.89	Found:	C	66.92	
		H	7.75		H	8.30	

Judged by the analysis, slight decomposition of the ozonide had already commenced. The ozonide was easily soluble in ether, ethyl acetate, acetone, acetic acid, benzene, carbon tetrachloride, and carbon disulfide. It was decomposed only very slowly by water, with formation of a resin.

Cleavage of the Ozonide by 3,6-Endomethylene Hexahydrohomophthalaldehyde.—Only a very small quantity of hydrogen was absorbed, by agitation in the presence

of platinum on silica gel, by an ethyl acetate solution of the ozonide prepared at -75° C. Since aluminum amalgam also attacked the ozonide only slowly, 4 grams of ozonide were dissolved in a little glacial acetic acid, and the solution was warmed with 3 grams of zinc dust. After one hour the excess of zinc dust was removed by filtering, and the acetic acid solution was diluted with water. It was then neutralized with sodium bicarbonate, extracted with ether, and the residue obtained by evaporation of the ether was distilled in a high vacuum. After distillation of a small quantity of initial distillate, the dialdehyde passed over at 112° C. (0.3 mm. pressure) as a colorless oil, which turned yellow fairly rapidly. By repeating the distillation, the dialdehyde was obtained in pure form.

Analysis

Substance:	5.150 grams:	CO ₂	13.632 mg.		
		H ₂ O	3.858 mg.		
C ₁₀ H ₁₄ O ₂ :	Calculated:	C	72.24	Found:	C 72.19
		H	8.50		H 8.38

On prolonged storage, the dialdehyde solidified, apparently as a result of polymerization to a vitreous mass.

Bis-2,4-Dinitrophenylhydrazone.—The dialdehyde was dissolved in 30 times its quantity of methyl alcohol, and to this solution was slowly added, with good agitation, a slight excess of a solution of 2,4-dinitrophenylhydrazine in sulfuric acid. After standing for 5 hours on a water bath, the flocculent hydrazone which separated was filtered and recrystallized several times from toluene. It formed orange-red needles, with melting point 212° C. (decomposition). It was slightly soluble in alcohol, and it gave a red color with potassium hydroxide in methyl alcohol.

Analysis

Substance:	4.373 grams:	CO ₂	8.170 mg.		
		H ₂ O	1.718 mg.		
	3.861 grams:	N	0.714 cc. (19° C., 739 mm.)		
C ₂₂ H ₂₂ O ₈ N ₈ :	Calculated:	C	50.17	Found:	C 50.95
		H	4.21		H 4.40
		N	21.29		N 21.02

In an attempt to prepare a semicarbazone from the dialdehyde, for which only a very small quantity was used, a white substance was obtained with melting point of 189° C. (from alcohol). It could not be purified further, but the nitrogen, determined by microanalysis, was 28.21%, compared with a value of 29.99% calculated for the disemicarbazone. Probably therefore the substance obtained was the compound sought for.

II

1. Titration of Sol Rubber with Bromine

The rubber required for these experiments was crepe extracted by acetone, and separated into its several fractions by standing extraction with ether. Sol fractions 2 and 3 were used for all the experiments.

A solution of 2.5 grams of rubber in 80 cc. of the purest chloroform was prepared, and was then ozonized at 0° C. with 5.5 per cent ozone. During ozonization, 5-cc. samples were removed and were titrated by the ten-minute procedure. The results are shown in Fig. 1. In every test, the rubber required somewhat more bromine than the theoretical amount, but this was of no significance, since it could be accounted for by differences in the introduction of the ozone (see II, 2, page 22).

In samples removed after the ozonization had been continued for only a short time, rubber bromide still precipitated during titration. As the time of treatment

increased, this precipitate became progressively smaller, and towards the end of the ozonization there was in most cases no longer any precipitation. The evolution of hydrogen bromide during the titration increased somewhat with the time of ozonization. When the last sample was removed, unconsumed ozone passed through the ozonizing tube. The "critical point" lay between the last and the next-to-last sample taken.

2. Titration with Pyridine Dibromide Hydrobromide

Preparation of the Solution.—The method of Rosenmund and Kuhnnehn was used to prepare pyridine dibromide hydrobromide,¹⁴ 0.05 mol of which was then dissolved in a mixture of 500 cc. of pure glacial acetic acid and 500 cc. of pure acetic anhydride. This solution was standardized by 0.1 N arsenite solution. To 20 cc. of 0.1 N arsenite solution were added 10 cc. of dilute hydrochloric or sulfuric acid and 30 cc. of water, and the solution colored pink with a few drops of aqueous methyl orange. Over a white background, the dibromide solution was added dropwise, with rotary agitation, until the pink color disappeared.

The double bonds were determined by allowing a solution of the substance in question to stand in glacial acetic acid, chloroform, or carbon tetrachloride and an excess of 10–20% dibromide for 5–10 minutes. After this, 30 cc. of water, 10 cc. of dilute sulfuric acid, and a quantity of 0.1 N arsenite solution somewhat in excess of that necessary for decolorizing the solution were added. The excess of arsenite solution was then titrated back, after addition of a few drops of methyl orange solution, with dibromide. In titrating rubber, it is necessary to add benzene to its chloroform or carbon tetrachloride solution to prevent flocculation of the rubber on addition of the dibromide solution. Only under these conditions does the procedure give satisfactory results.

Analysis

Rubber: 0.0817 g., 0.1 N dibromide solution	23.90 cc. (calculated 24.03)
0.0917 g., 0.1 N dibromide solution	27.0 cc. (calculated 27.20)

Rubber can be titrated much better with pyridine dibromide hydrobromide than with free bromine, because in the latter case substitution always takes place. In view of this, neither the bromine nor the iodine chloride method was used in the present investigation.

In preparing the solution of ozonized rubber to be titrated, 2 grams of rubber were ozonized in 90 cc. of chloroform at 0° C. with 5.5% ozone. Samples of 5 cc. were removed from the resulting solution (see Fig. 3).

After 210 minutes ozone passed in small quantities through the chloroform solution. At this point the solution, which no longer reacted with dibromide, consumed 27.60 cc. of 0.1 N bromine solution on titration with the latter. After ozonization for 4 minutes longer, the consumption diminished to zero. The critical point in this ozonization was therefore reached after 210 minutes.

3. Determination of the Hydrogen Bromide Liberated in the Titration of Sol Rubber with Bromine

To decide whether substitution takes place during bromination of the primary ozonide, it was necessary to determine the quantity of hydrogen bromide liberated. To this end the following procedure was followed.

The chloroform solution to be brominated was placed in a long-neck round flask, of 100 cc. capacity, into which a capillary was introduced through a tube attached to the side of the flask. A glass tube 2 cm. in diameter was connected with the flask by a ground-glass joint, and this tube had a stopcock, with very large bore, about 5 cm.

above the ground-glass joint. At a point 2 cm. above this stopcock was a burette attached with a rubber stopper so that the bromine solution which it contained could be dropped directly into the flask. Between the stopcock and the ground-glass joint was a delivery tube inclined downward, to which were connected in series a short tube containing phosphorous pentoxide, three wash bottles, a Wulff bottle, and a water jet pump. The first of the wash bottles was empty, the other two contained 20–40 cc. of 0.1 *N* silver nitrate solution.

In carrying out a determination, the large stopcock was closed after complete decoloration of the bromine solution, and the hydrogen bromide formed was drawn by means of the water jet pump into the silver nitrate solution. This required 30 minutes. In all determinations, suction was continued for just 45 minutes. The unconsumed silver nitrate was titrated back with 0.1 *N* potassium thiocyanate. In most cases the silver nitrate solution in the second wash bottle remained perfectly clear. Experiments on the bromination of phenol gave convincing evidence that if the experimental procedure described above is followed, the determination of hydrogen bromide is quite reliable.

Since in the titration of pure rubber in chloroform 20 per cent more bromine than the calculated quantity was consumed, the hydrogen bromide formed was determined in this case also.

Two Experiments.—0.1880 gram and 0.1892 gram of rubber, in each case in 15 cc. of chloroform, consumed 66.24 and 66.39 cc., respectively, of 0.1 *N* bromine solution, *i. e.*, 119.8 and 119.3 per cent, respectively, of the theoretical values. In the hydrogen bromide determination, 11.50 and 11.28 cc., respectively, of 0.1 *N* silver nitrate solution were used. Accordingly 54.74 and 55.11 cc., respectively, of 0.1 *N* bromine solution, *i. e.*, 99.00 and 99.03 per cent, respectively, of the theoretical values, of the corresponding quantities of bromine remained firmly combined.

In the main experiment, 8.5 grams of rubber were dissolved in 300 cc. of chloroform and ozonized at 0° C. with 5.5% ozone. Each 5 cc. removed was brominated in the apparatus described above, and at the same time hydrogen bromide was determined. Table III shows that the quantity of the latter increased gradually with increase in the time of ozonization.

TABLE III

Time of Ozonization (Min.)	Volume of 0.1 <i>N</i> Bromine (Cc.)	Volume of 0.1 <i>N</i> Silver Nitrate (Cc.)	Percentage of Hydrogen Bromide
0	50.58	8.43	16.67
25	47.26	7.18	15.19
55	45.32	7.50	16.55
85	45.03	8.55	18.99
115	44.57	9.54	21.40
155	45.33	11.90	26.26
225	44.91	13.32	29.64
231	0	0	0

To determine whether the primary ozonide reacted with hydrogen bromide, 1.2 grams of rubber in 80 cc. of chloroform was ozonized at 0° C. with 5.5 per cent ozone to the critical point. Twenty cc. of the resultant solution were added to 10 cc. of chloroform, in which 0.2306 gram of hydrogen bromide had been dissolved. Soon after the two solutions were mixed, the resultant solution turned yellow, and on standing this color became progressively more intense. After one hour the hydrogen bromide still present was determined in the usual way. It amounted to 0.1476 gram, which corresponds to a consumption of 36 per cent of the hydrogen bromide by the ozonide.

4. Reduction Cleavage of the Brominated Primary Ozonide by Sulfur Dioxide

After various attempts to obtain either the brominated ozonide or its cleavage fragments had failed, cleavage was successfully carried out with sulfur dioxide.

Rubber (8.3 grams) was dissolved in 300 cc. of pure chloroform, and was ozonized with 5.5% ozone to the critical point, while cooling by a freezing mixture. A solution of 22 grams of bromine in 50 cc. of chloroform was added slowly, cooling with ice. After the color of the bromine had disappeared, the main part of the chloroform was removed at 0° C. in a high vacuum. The yellow-brown residue was dissolved in 150 cc. of ether and treated with 30 cc. of water. To carry out the reduction, sulfur dioxide was passed into the ice-cold solution of the ozonide, with vigorous stirring, until hydrogen peroxide could no longer be detected. The ether solution was then neutralized with sodium bicarbonate, and dried with sodium sulfate. Distillation of the ether left a dark brown oil, from which hydrogen bromide was easily liberated. This oily residue was probably bromolevulinic aldehyde, but no attempts were made to isolate it.

The aqueous solution and the sodium bicarbonate solution were acidified with hydrochloric acid, whereby a small quantity (0.18 gram) of a substance was precipitated. After drying, this substance was recrystallized from benzene. Its melting point was 115° C., and analysis showed it to be β -dibromolevulinic acid.

By repeated extraction with ether, drying, and evaporation, the filtrate yielded β -bromolevulinic acid, which after evaporation of the ether and long storage in a vacuum desiccator, solidified, with a yield of 7.87 grams. After recrystallizing several times from ligroin, it fused at 55° C. As a means of identification, it was converted into β -acetylacrylic acid by warming with sodium acetate in glacial acetic acid, and the β -acetylacrylic acid was easily identified by its hitherto unknown *di-nitrophenylhydrazone*.

To this end an aqueous solution of β -acetylacrylic acid was treated with a slight excess of a sulfurous acid solution of 2,4-dinitrophenylhydrazine. The flocculent precipitate was allowed to stand for a short time, and was then filtered and recrystallized from glacial acetic acid. It formed orange colored small rods, with melting point of 257° C. (decomposition). It colored a solution of potassium hydroxide in methyl alcohol red.

Analysis

Substance:	3.430 grams:	N	0.583 cc. (26° C., 742 mm.)
$C_{11}H_{16}O_6N_4$:	Calculated:	N	19.05
	Found:	N	18.96

5. Behavior of Rubber Oxide towards Bromine

To determine whether rubber oxide reacts with bromine in the same way that the primary ozonide does, definite weights of rubber were dissolved in chloroform and let stand at 0° C. for 48 hours with perbenzoic acid. The solutions were then titrated in the usual way with 0.1 N bromine solution. In this way it was proved that the only solutions which consumed bromine were those in which the compound still contained unchanged double bonds because of a deficiency of perbenzoic acid. The consumption of bromine corresponded to the number of double bonds which were not saturated by perbenzoic acid.

Experiment 1.—0.1351 gram of rubber was dissolved in 15 cc. of chloroform, 0.3765 gram of perbenzoic acid (137.3 per cent of the theoretical proportion) was added, and the mixture was allowed to stand for 48 hours at 0° C. At the end of the 48 hour period, no more bromine was consumed.

Experiment 2.—0.1351 gram of rubber was treated with 0.2510 gram (95.21 per

cent of the theoretical proportion) of perbenzoic acid under the same conditions as Experiment 1. 0.81 cc. more of 0.1 *N* bromine solution (2.12 per cent of the theoretical proportion) was consumed. Altogether therefore 97.33 per cent of the double bonds reacted.

Experiment 3.—0.1004 gram of rubber and 0.1555 gram of perbenzoic acid (73.6 per cent of the theoretical value) were used. For this mixture 7.56 cc. of 0.1 *N* bromine solution (25.60 per cent of the theoretical quantity) were consumed. Altogether therefore 101.90 per cent of the double bonds reacted.

III

1. Experiments on the Reduction of the Primary Ozonide

(a) *With Zinc Dust.*—Rubber (4.2 grams) in 200 cc. of chloroform was ozonized at 0° C. with 5.5% ozone to the critical point. The chloroform was then removed in a vacuum not above 20° C., and the pale yellow, very viscous residue dissolved in 150 cc. of ethyl acetate. To this solution were added, with vigorous stirring, 12 grams of zinc dust, 0.1 gram of silver nitrate, 0.1 gram of hydroquinone and 30 cc. of water. After 3 hours iodine was no longer precipitated from potassium iodide solution. The solution was then freed of excess zinc dust, and extracted twice with sodium bicarbonate solution. After drying the ethyl acetate solution with sodium sulfate, the ethyl acetate was distilled, the residue was dissolved in alcohol and was precipitated with dinitrophenylhydrazine. The precipitated substance fused at 209–214° C. (with decomposition), and was very difficultly soluble in alcohol. After recrystallization once from a mixture of pyridine and alcohol, it fused at 230° C. A mixture with synthetic levulinic aldehyde-*bis*-2,4-dinitrophenylhydrazone did not depress the melting point. In this experiment 5.5 grams of hydrazone were obtained, which corresponds to a 19.7 per cent yield of levulinic aldehyde.

A part of the sodium carbonate solution, which contained the acid cleavage products, was acidified with dilute sulfuric acid, and likewise precipitated with 2,4-dinitrophenylhydrazine. This precipitate consisted solely of the hydrazone of levulinic acid, with melting point of 203° (with decomposition). Calculated on a basis of the total quantity of sodium bicarbonate solution, the yield of levulinic acid was 48.8 per cent of the carbon skeleton.

Extraction of the filtered zinc dust by alcohol and dioxan gave no indication that a polyglycol could have been formed in the reduction. It dissolved in dilute sulfuric acid without leaving any residue.

(b) *Catalytic Hydrogenation.* *Experiment 1.*—Rubber (2.2 g.) in 100 cc. of chloroform was ozonized at 0° C. to the critical point, and then agitated at 19° C. in the presence of 0.4 g. of platinum on silica gel²⁸ with hydrogen. At the end of 16 hours, 282 cc. of hydrogen had been absorbed, *i. e.*, 39.2 per cent of the theoretical quantity. Further addition of catalyst had no effect whatever. A slight oxidizing action of the chloroform solution towards hydrogen iodide still existed. After extraction with sodium bicarbonate solution, the pale yellow chloroform solution was dried with sodium sulfate. The chloroform was then distilled on a water bath, and the residue was distilled in a vacuum. After a very small quantity of distillate had passed over, the temperature rose quickly to 68° C., and at 68–71° C. (13 mm. pressure) 0.85 gram of a colorless liquid passed over. Thereafter there was no further distillate, even when the temperature of the oil bath was raised to 150° C.

The fraction obtained at 68–71° C. was pure levulinic aldehyde, as was proved by the preparation of its *bis*-dinitrophenylhydrazone. The yield was 26.6 per cent of the carbon skeleton. An attempt to benzoilate the residue from the distillation was fruitless, for no polyglycol was present. The yield of levulinic acid was 46.2 per cent (determined by precipitation as dinitrophenylhydrazone).

Experiment 2.—The same procedure was followed as in the first experiment, with 4.7 grams of rubber. For no evident reason the hydrogenation was less successful; and only 27.8 per cent of the theoretical quantity of hydrogen was absorbed. The yield of levulinic aldehyde was correspondingly lower, *viz.*, 18.81 per cent of the carbon skeleton. The yield of levulinic acid was 53.9 per cent.

Rubber (7.5 grams) in 220 cc. of chloroform was ozonized at 0° C. to the critical point. The chloroform was then distilled, first in an ordinary vacuum, then in a high vacuum, and the residue was dissolved in 110 cc. of ethyl acetate. To the solution was added 0.6 gram of platinum on silica gel and the mixture was agitated with hydrogen. At the end of 23 hours 1192 cc. of hydrogen had been absorbed, *i. e.*, 25 per cent of the theoretical amount. The ethyl acetate solution was a pale yellow color. The ethyl acetate was distilled on a water bath. To obtain any polyglycol which might be present, the levulinic aldehyde was distilled with steam, and the residue was treated with dilute sodium hydroxide and benzoyl chloride. A small amount of benzoic anhydride was obtained, but nothing to indicate the presence of a polyglycol.

2. Isolation of the Primary Ozonide

A solution of rubber in chloroform ozonized at 0° C. to the critical point was concentrated in a vacuum, at a temperature not exceeding 20° C. The very pale yellow, oily residue was dissolved in a little ethyl acetate, and was then precipitated by slow addition of low-boiling petroleum ether. After this operation had been repeated five times, the ozonide was freed of solvent over phosphorous pentoxide in a high vacuum; it then solidified to a vitreous mass.

Analysis

Substance:	5.248 grams:	CO ₂	9.978 mg.				
		H ₂ O	3.348 mg.				
(C ₅ H ₈ O ₃) _n :	Calculated:	C	51.70	Found:	C	51.85	
		H	6.95		H	7.14	
Substance:	0.1850 gram:	Cryoscopic molecular weight in 52.786 grams of bromoform $\Delta = 0.087^\circ$					
(C ₅ H ₈ O ₃) ₅ :	Calculated:	580		Found:	580		

This ozonide softened at 35° C., and at 45° C., gas commenced to be evolved, and increased with rise in temperature. It was insoluble in ether, carbon tetrachloride, carbon disulfide, and petroleum ether; soluble in benzene, alcohol, and acetone; and very easily soluble in glacial acetic acid, ethyl acetate, and dioxan.

In the titration with bromine, this ozonide still required 0.91 mol of bromine per C₅H₈O₃ unit. In some cases the consumption of bromine was considerably smaller, without any apparent reason.

Experimental.—0.1510 gram and 0.1276 gram, respectively, of ozonide in 10 cc. of chloroform consumed 23.75 cc. and 20.00 cc., respectively, of 0.1 N bromine, *i. e.*, 91.27 and 90.98%, respectively, of the theoretical amount.

3. Unsuccessful Attempts to Transform the Ozonide Unstable towards Bromine into the Ozonide Stable towards Bromine

When oxygen containing no ozone was passed for a long time through a solution of ozonide at the critical point, there was no diminution in the bromine consumption, whereas introduction of ozone for only a few minutes rendered the solution stable towards bromine. Introduction of phosgene into a solution of the primary ozonide did not change the consumption of bromine. Also after prolonged treatment with dry hydrogen chloride a solution of the primary ozonide decolorized just as much

bromine as before treatment. Apparently hydrogen chloride does not react so quickly with the ozonide as does hydrogen bromide.

Likewise with nitrogen dioxide, there was no rearrangement. By treatment of the primary ozonide in solution with nitrogen dioxide which had been dried with phosphorous pentoxide, a small quantity of a flocculent precipitate was formed, but this gradually redissolved. Probably under these conditions the ozonide undergoes oxidation.

When a solution of the ozonide at the critical point was allowed to stand with iodine, and the latter was subsequently removed by agitating with silver in powdered form, the resultant solution reacted with the same quantity of bromine as before treatment.

Likewise the bromine consumption of a solution of the primary ozonide was not diminished by addition of acids such as glacial acetic acid, trichloroacetic acid, and benzoic acid.

With antimony pentachloride and with stannic chloride, the primary ozonide reacted even in dilute solution, with turbulent evolution of hydrogen chloride.

Exposure of a solution of the primary ozonide to ultra-violet radiation for several hours did not reduce the consumption of bromine.

Finally the primary ozonide was not transformed into the ozonide stable towards bromine by treatment with benzoyl peroxide, levulinic acid peroxide, or di- and tri-molecular acetone peroxide.

4. Loss of Power of Bromination by Treatment with Perbenzoic Acid

(a) *The Primary Ozonide of Rubber.*—In a series of experiments different quantities of a solution of perbenzoic acid in chloroform were added to the same volume of a solution of the primary ozonide. Then equal volumes of bromine solution were added to each of the products, and the times required for the color of the bromine to disappear were determined. The results are summarized in Fig. 6; the quantities of perbenzoic acid and bromine added are based on the base mol.

The last two samples might be considered to be stable towards bromine, as judged by titration by the ten-minute procedure. When more bromine was added after complete consumption of the bromine solution originally added, the additional bromine was rapidly decolorized. On the other hand, when more perbenzoic acid was added at the same time, the retarding action of this acid was again evident.

Experimental.—To 10 cc. samples of a solution of rubber ozonide in chloroform (0.512 gram of ozonide) different quantities of a chloroform solution of perbenzoic acid were added, each solution was treated with 2 cc. of a solution of bromine (0.0518 gram of bromine) in carbon tetrachloride, and the times required to consume this quantity of bromine were observed. Then in every case the same quantity of bromine was again added, and the times required for decolorization were again determined.

Perbenzoic Acid (Mol)	Bromine (Mol)	Time for Decolorizing the First Bromine Added (Min.)	Time for Decolorizing the Second Bromine Added (Min.)
0.019	0.074	9	A few seconds
0.038	0.074	22	A few seconds
0.076	0.074	78	10
0.114	0.074	149	28
0.152	0.074	235	63

(b) *Acetone.*—In a first series of experiments the same quantities of a solution of acetone in chloroform (5.558 grams of highly purified acetone made up to 100 cc. with pure chloroform) were mixed with various quantities of a solution of perbenzoic acid. After addition of the same quantity of bromine to each of the solutions,

the lengths of time that the color of the bromine persisted in the different solutions were determined. Figure 4 shows that the time required for decolorization increased with increase in the quantity of perbenzoic acid added. Here, too, bromine added after decolorization of the original bromine was consumed rapidly. The quantities of bromine and of perbenzoic acid are based on one mol of acetone. In a second series of experiments, twice as much perbenzoic acid and bromine were added.

Experimental.—To a solution (10 cc.) of acetone in carbon tetrachloride (0.795 gram of acetone) were added 2 cc. of a chloroform solution of perbenzoic acid (0.1034 gram) and 6 cc. of a carbon tetrachloride solution of bromine (0.155 gram). The mol proportions were therefore:

$$\text{acetone} : \text{perbenzoic acid} : \text{bromine} = 1 : 0.055 : 0.063$$

At the end of 112 minutes the solution had become colorless. The hydrogen bromide was eliminated by agitation with silver carbonate and filtration. To one-half (9 cc.) of the filtrate, 1 cc. of perbenzoic acid solution and 3 cc. of bromine solution were added. The color of the bromine disappeared only after 10 hours.

Behavior of Acetone towards Bromine in the Presence of Hydrogen Bromide

To 10 cc. of a solution of acetone (0.795 gram) in carbon tetrachloride were added 1 cc. of a chloroform solution of hydrogen bromide (0.0349 gram) and 1 cc. of a carbon tetrachloride solution of bromine (0.0259 gram). The color of the bromine disappeared after a few seconds, whereas without hydrogen bromide it persisted for about 20 minutes.

(c) *Ethyl Acetoacetate.*—To 5 cc. samples from a solution of 5.115 grams of ethyl acetoacetate made up to 100 cc. with chloroform were added various quantities of perbenzoic acid solution. Then in every case the same quantity of bromine was added, and the times required for the color of the bromine to disappear were observed. In Fig. 5 all values are based on 1 mol of ethyl acetoacetate. In all cases further additions of bromine were quickly decolorized.

The retardation of bromination was also evident when a bromine solution containing perbenzoic acid was added to the solution of the substance to be brominated. Neither with ethyl acetoacetate nor with the primary ozonide was it necessary for the perbenzoic acid to react for a long time before the bromination.

(d) *Behavior of Perbenzoic Acid towards Hydrogen Bromide in Chloroform.*—

1. Ten cc. of a solution of hydrogen bromide (0.3492 gram) in chloroform and an excess of perbenzoic acid (5 cc. = 0.2083 gram of acid) were allowed to stand for 3 minutes, the precipitated bromine was removed with silver powder, and, after filtering, the solution was tested for perbenzoic acid by potassium iodide. It was completely consumed.

2. Five cc. of the hydrogen bromide solution above (0.1746 gram of hydrogen bromide) and 5 cc. of perbenzoic acid (0.2083 gram) solution were allowed to stand for 3 minutes; after elimination of the liberated bromine as in Experiment 1, and addition of potassium iodide and dilute sulfuric acid to decolorize the separated iodine, 8.13 cc. of 0.1 *N* thiosulfate were still consumed; this corresponds to 0.0561 gram of perbenzoic acid. A weight of 0.0594 gram was expected for a quantitative transformation.

3. Five cc. of hydrogen bromide solution (0.1746 gram of hydrogen bromide) and 7.5 cc. of perbenzoic acid solution (0.3124 gram of perbenzoic acid) were allowed to stand for 3 minutes; after treatment as in Experiment 2, 23.04 cc. of 0.1 *N* thiosulfate (0.1590 gram of perbenzoic acid) were consumed. Theoretically 0.1635 gram of perbenzoic acid was to be expected.

IV

Preparation of a Difficultly Soluble Ozonide of Rubber

Experiment 1.—Into a solution of 3 grams of rubber in 80 cc. of carbon tetrachloride at 0° C. a deficiency, viz., 60 per cent of the theoretically necessary quantity of ozone was passed. Soon after the beginning of ozonization a flocculent precipitate separated, and the quantity of this precipitate increased progressively. It was separated, thoroughly washed with ether and petroleum ether, and freed of solvent in a high vacuum. The product softened at 75° C., and at 85° C. gas began to be evolved, without the substance showing any true tendency to fuse before this decomposition.

Analysis

Substance:	5.075 grams:	CO ₂	9.618 grams	H ₂ O	3.231 grams
	5.421 grams:	CO ₂	10.310 grams	H ₂ O	3.251 grams
(C ₅ H ₈ O ₃) _n :	Calculated:	C	51.70	H	6.95
	Found:	C	51.69	H	7.12
			51.87		6.71

When the experiment was repeated, the precipitated ozonide agglomerated very strongly and, in spite of careful and thorough washing with ether and petroleum ether, the absorbed carbon tetrachloride could not be completely removed. The product was therefore allowed to swell in ethyl acetate, in which the normal ozonide dissolves easily, and was then precipitated by petroleum ether. The results of analysis then agreed with the previous ones.

Analysis

Molecular weight determination (cryoscopic in bromoform)

Substance: 0.1311 gram: Cryoscopic molecular weight in 47.365 grams of bromoform $\Delta = 0.069^\circ \text{C}$.

(C₅H₈O₃)_n: Calculated: 580
Found: 577.5

In contrast to the ozonide prepared in chloroform, this ozonide was very difficultly soluble in chloroform, bromoform, benzene, and ethyl acetate. Furthermore it consumed only relatively little bromine. Thus 0.1448 gram of ozonide in 20 cc. of chloroform consumed 4.65 cc. of 0.1 N bromine solution, i. e., 18.64 per cent of the theoretical quantity.

The ozonide prepared in chloroform reacted with the iodide ion more rapidly and to a greater extent than does the ozonide prepared in carbon tetrachloride.

Experimental. Ozonide from chloroform.—0.1793 gram and 10 cc. of a solution of potassium iodide in 10% sulfuric acid were allowed to stand for 90 minutes. Consumption: 6.14 cc. of 0.1 N sodium thiosulfate per mol of ozonide; 0.199 mol of iodine. *Ozonide from carbon tetrachloride.*—0.1868 gram consumed in like manner 2.10 cc. of 0.1 N sodium thiosulfate, corresponding to 0.065 mol of iodine.

Another experiment was directed towards establishing the relation between the quantity of ozonide precipitated and the quantity of ozone passed into the solution.

Rubber (4 grams) in 80 cc. of carbon tetrachloride was ozonized at 0° C with 5.5 per cent ozone. After introduction of 61 per cent of the ozone theoretically necessary the ozonization was stopped, the flocculent precipitate was filtered with suction and was washed thoroughly with ether. The part of the precipitate which adhered tenaciously to the walls and to the delivery tube of the ozonizing chamber was dissolved in ethyl acetate, the solution was concentrated in a vacuum, and the substance was precipitated with petroleum ether. In this way, a total of 2.77 grams of

solid ozonide was collected. This quantity corresponded to a yield of 66.6 per cent, based on the ozone introduced.

The filtrate from the solid ozonide was concentrated in a vacuum and, when acetone was added, a tough mass separated. This was separated, was allowed to swell in ether, and was precipitated with acetone. After repeating this operation four times, the substance was obtained in the form of a pale yellow mass, the general characteristics of which resembled those of rubber. This was confirmed in an approximate way by analysis, in that a carbon deficiency of only 2.75 per cent was found, and admixture of the previously dissolved ozonide is not at all impossible.

Analysis

Substance:	5.530 grams:	CO ₂	17.317 mg.		
		H ₂ O	5.490 mg.		
(C ₈ H ₈) _x :	Calculated:	C	88.15	H	11.85
	Found:	C	85.40	H	11.11

The yield of this product was 0.61 gram, *i. e.*, 15.2 per cent of the starting substance. The remainder of the latter was apparently more strongly oxidized, and therefore had probably been rendered soluble in acetone.

Acknowledgment

Appreciation is due the Deutsche Forschungsgemeinschaft for promoting this investigation, and Rich. Meister for making the microanalyses.

References

- ¹ The present article continues in more comprehensive form a previous article which was published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. X, No. 1, pages 114-119, January, 1937, and which represents an earlier address by Pummerer in München.
- ² Harries and Türk, *Ann.*, **374**, 342 (1910).
- ³ *Ann.*, **374**, 303 (1910).
- ⁴ *Ber.*, **58**, 1088 (1925).
- ⁵ More recently Staudinger has considered molozonides as reaction products, with free reactive points, which are incapable of continuous existence, but which by a chain reaction form polymeric ozonides as mixed polymers from ozone and the unsaturated compound. See RUBBER CHEM. & TECH., **10**, 114 (1937).
- ⁶ *Ber.*, **65**, 1274 (1932).
- ⁷ Pummerer, Matthäus, and Socias-Viñals, Address at the 9th International Congress of Pure and Applied Chemistry, Madrid (Vol. IV of the Reports of the Congress). See also *Z. angew. Chem.*, **47**, 366 (1934).
- ⁸ *Ber.*, **34**, 2979 (1901).
- ⁹ *Ber.*, **65**, 1471 (1932).
- ¹⁰ This apparatus, which may be of utility in other ways, has been designed by Matthäus and one of the present authors, and has been constructed by the firm of K. F. Heinz in Stützerbach (see Experimental Part).
- ¹¹ Staudinger, *Ber.*, **58**, 1095 (1925).
- ¹² This point of view was taken in the address of Pummerer at the 9th International Congress of Pure and Applied Chemistry at Madrid. See also Note 7.
- ¹³ This experiment was carried out by Gerd. Richter.
- ¹⁴ *Ber.*, **56**, 1263, 2042 (1923); *Z. angew. Chem.*, **37**, 58 (1924).
- ¹⁵ *Ber.*, **55**, 3485 (1922).
- ¹⁶ *Ber.*, **64**, 811 (1931).
- ¹⁷ *Ann.*, **486**, 83 (1931).
- ¹⁸ *Kautschuk*, **21**, 198 (1936).
- ¹⁹ In the particular case of acetone, an acceleration of enolization by hydrogen bromide may likewise play a part in the result.
- ²⁰ This subject is treated comprehensively by Schumacher, *Z. angew. Chem.*, **49**, 613 (1936).
- ²¹ Harries, "Das Ozon," Berlin, 1916, p. 671; E. Paulsen, *Dissertation*, Kiel, 1910.
- ²² *Ber.*, **41**, 3552 (1908).
- ²³ *Ber.*, **58**, 1088 (1925).
- ²⁴ *Ber.*, **32**, 1326 (1899).

²⁵ According to Slawinski (*Chem. Zentr.*, **1918**, 915), this compound forms no crystalline derivative with phenylhydrazine or semicarbazide. For information on the glycol, see Pastureau and Bernard, *Chem. Zentr.*, **1924**, 1667; Harries and Pappos, Note 2.

²⁶ The apparatus was supplied by the firm of Wilh. K. Heinz of Stützerbach.

²⁷ This apparatus has proved to be very satisfactory in our laboratory. The ozonizer is placed in a hood with several groups of 2-3 ozonizing units arranged in parallel, from which fused glass tubes lead to the main apparatus on ordinary laboratory tables nearby. From here an iron exhaust tube leads back through the hood, and thence directly into the open air rather than into the flue of the hood.

²⁸ Catalyst No. 17 of the Membranfiltergesellschaft, Göttingen.

X-ray Diffraction Patterns of Sol, Gel, and Total Rubber when Stretched, and when Crystallized by Freezing and from Solutions

George L. Clark,* Enno Wolthuis,† and W. Harold Smith

I. INTRODUCTION

When unstretched rubber is examined by x-rays, it produces a blurred ring, the halo of which is typical of the amorphous or liquid state. Its behavior when stretched was first reported by Katz,¹ who observed interference spots at 80 per cent elongation. Their intensity increased with increasing elongation, and at 400 per cent a definite fiber diagram was observed. Consequently rubber, when extended, was considered to be crystalline, and the Joule effect to result from an actual formation of crystals. When Katz heated stretched rubber, the interference spots vanished. Vulcanized rubber produced interferences, but the spots were weaker than those obtained with unvulcanized rubber. The identity period along the direction of stretch was 8 A. U., and the dimensions assigned to the unit cell were $8 \times 6.5 \times 6.5$ A. U., with a volume of 338 (A. U.)³.

The behavior of stretched rubber between 80 and 1000 per cent elongations was investigated by Hauser and Mark,² who made a more accurate study of the positions and intensities of the interferences. The positions of the interferences were found to be independent of the degree of stretching, but their intensities increased proportionally with it. The position of the amorphous ring remained unchanged during extension, but its intensity decreased with continued elongation. Therefore an amorphous or liquid phase in unstretched rubber was supposed to be changed to a crystalline phase when it was stretched. The positions of the interferences, which depend on the dimensions of the unit cell, did not change with continued stretch, and consequently a definite space lattice was indicated. Other evidence showed that new crystalline units were constantly produced during elongation, and that the major axis of the crystalline phase was oriented parallel to the direction of stretch. The interferences in stretched rubber disappeared at 60° C. When rubber was maintained in an extended condition for some time, the interference spots vanished. If rubber was milled or swollen by solvents before stretching, the interference spots did not appear. An orthorhombic configuration was assigned to the unit cell, but the possibility of a monoclinic structure was admitted. Its dimensions, $8.0 \times 8.6 \times 7.68$ A. U., correspond to a cell volume of 529 (A. U.)³. There were 4.12 molecules of C_5H_8 per unit cell.

The interferences obtained by Mark and von Susich³ were better defined, and better measurements were possible. A rhombic cell was assumed and the dimensions given to it were $8.3 \times 8.1 \times 12.3 \pm 0.1$ A. U. The volume of the unit cell was reported to be 830 ± 30 (A. U.)³, with 7.1 molecules and not 8, presumably because

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† Graduate Student, University of Illinois. A part of the material in this paper was presented as a thesis by Enno Wolthuis in May, 1937, to the Faculty of the Graduate School of the University of Illinois, represented by George L. Clark, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

of poor density values. With the Weissenberg apparatus, Mark and von Susich proved that the indices (111) and (200) of Hauser and Mark are really (100) and (010). They observed that very thin specimens of rubber showed fibering and also three-dimensional orientation. So a distribution of carbon atoms was proposed which aims to reconcile the orientation of the primary valence chains in the direction of stretch, atomic spacings for single and double-linked carbon atoms, and the observed intensities. By topochemical reactions, they attempted to convert stretched rubber into derivatives retaining the structure, but x-ray patterns of the derivatives indicated an amorphous condition.

On the basis of a single experiment, Ott⁴ assigned a volume of 259 (A. U.)³ to the largest possible cell. Using the values of Bragg for the radius of carbon, 0.77 A. U. and of hydrogen, 0.73 A. U., and assuming close packing, the volume of C₅H₈ was computed to be 43.1×10^{-24} ml. or 43.1 (A. U.)³. On these assumptions, the maximum number of C₅H₈ groups in Ott's cell is six.

A recent paper by Lotmar and Meyer⁵ reports accurate measurements of the structure of crystallized rubber. The unit cell was derived by the graphical method of Sauter, is monoclinic, and has the following axes:

$$\begin{aligned} a &= 8.54 \pm 0.05 \text{ A. U.} \\ b &= 8.20 \pm 0.05 \text{ A. U. (fiber axis)} \\ c &= 12.65 \pm 0.05 \text{ A. U.} \\ \beta &= 83^\circ 20' \end{aligned}$$

$$\text{Volume of unit cell} = 880 \text{ (A. U.)}^3, \text{ approximately.}$$

They report 7.6 molecules per unit cell, and this value is based on the highest value of density, 0.965, reported in the literature.⁶ Eight molecules are assumed to be present. By an elimination of possible space groups, there remains the probable one, C_{2h}, and the chains are presumed to have the symmetry of a twofold screw axis. The crystallite is said to be a molecular racemate of right and left spiral molecules.

Subsequent to the work of Lotmar and Meyer, Barnes⁷ examined two samples of frozen crude rubber, one of which had remained frozen for 22 years, and the other for at least 11 and probably for 30 years. They lost their opacity at approximately 41° C. The measurements of Barnes agree excellently with those reported by Lotmar and Meyer for stretched rubber. Identical patterns were obtained from each specimen.

Crystal interferences in frozen, unstretched smoked sheet were found by Hauser and Rosbaud.⁸ They were indicated by Debye-Scherrer rings. Later, von Susich⁹ constructed a melting curve from the behavior of patterns of frozen rubber at different temperatures. With unstretched rubber, the powder pattern disappeared completely at approximately 35° C., and with stretched rubber at about 90° C. Above 90° C. the pattern was that of an amorphous material. Indices were assigned to four rings in the frozen-rubber pattern, but no spacings or calculations were mentioned.

In the present investigation the work of Lotmar and Meyer is checked with stretched gel rubber, which yields a sharper and more intense diffractive pattern than is obtained with the total rubber. The powder patterns of frozen sol, gel, and total rubbers are compared as to their interplanar spacing and the intensity of their interferences, and an examination is made of the sol and gel fractions crystallized from an ethereal solution at low temperature.

II. MATERIALS AND METHODS

The rubber hydrocarbon used in this investigation was obtained from the latex of *Hevea brasiliensis*, the source of the principal rubber of commerce. It was pre-

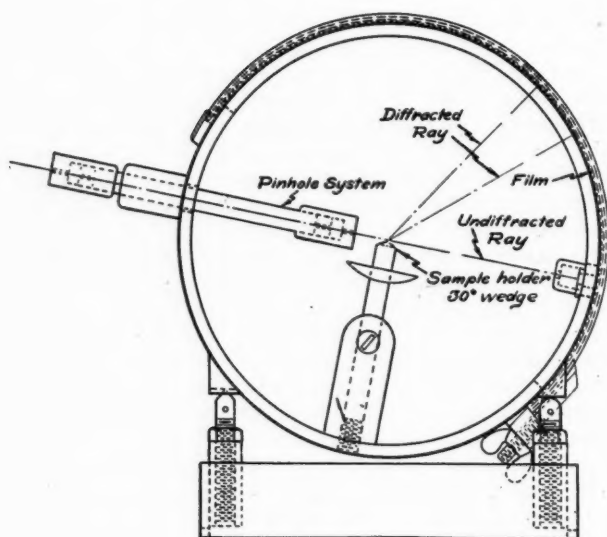


Figure 1—Cylindrical Camera

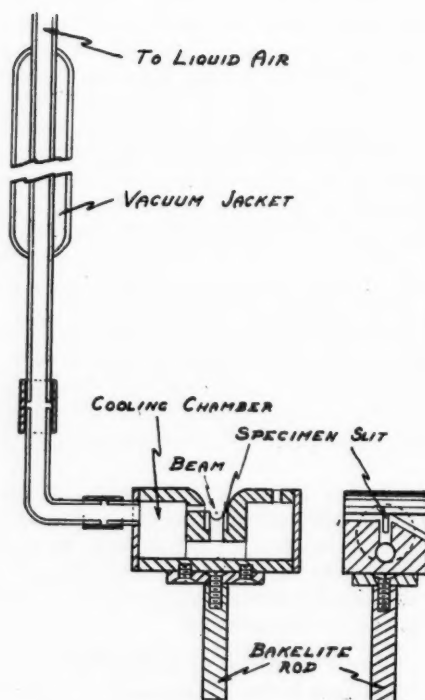


Figure 2—Low-Temperature Specimen Holder

pared at the National Bureau of Standards from latex supplied by the United States Department of Agriculture, and was studied by x-rays at the University of Illinois.

The preparation of pure sol, gel, and total rubber hydrocarbons, and the formation of discrete crystals of sol and gel rubber from solution, have been discussed in previous issues of this journal.¹⁰ Similar material was used in this investigation. The rubber was purified and separated into sol and gel fractions under conditions which aimed to preserve its structure and to avoid the effects of light and of oxygen. Oxidation of the rubber was minimized by allowing it to remain in contact with the natural antioxidants, which are in crude Hevea rubber, until the final stage of purification. At low temperatures the hydrocarbons in massive rubber crystallize without a solvent. Specimens of "frozen" sol and gel were prepared by maintaining the samples at -25°C . for 30 days. Other specimens of crystalline sol and gel rubber were prepared at low temperatures from ethereal solutions of the fractions.

The production of a diffraction pattern by stretched rubber, and the changes which occur when unstretched rubber is frozen and when it separates from an ethereal solution at low temperatures as discrete particles have been repeatedly termed crystallization, and that word will be used in this paper.

In the application of the ordinary x-ray diffraction equipment and technic, there is no resolution of interferences which correspond to the very long interplanar spacings which frequently exist in natural materials. Hence, special apparatus and methods have been developed in the x-ray laboratory of the University of Illinois, in which a magnetic field is used to deflect the scattered electrons which ordinarily fog the film. Definite and reproducible evidence has been obtained of very large spacings in collagen, gelatin, keratin, and other materials, including gel rubber.

For the work with stretched gel rubber an ordinary flat-film camera was used. The distance from specimen to film was 5 cm. For the work with frozen sol, gel, and total rubbers, and rubber crystals deposited from solution, special apparatus and technic were again required to obtain the diffraction patterns at temperatures below the melting point of the crystals.

The crystallized rubber specimens were examined by two specially constructed types of cameras. One was a cylindrical camera, shown in Fig. 1, in which a low-temperature specimen holder, pictured in Fig. 2, was inserted in place of the wedge sample holder used for powder specimens. The entire holder was cooled by the exhaust from a liquid-air reservoir, and the cold air passed out alongside the specimen. The sides of the cylindrical camera were closed to prevent condensation of moisture on the specimen. The air in the camera was readily precooled by placing solid carbon dioxide within it. The other low-temperature camera is shown in Fig. 3, and had the advantage of a longer distance from specimen to film for the accurate determination of the longer spacings. It consisted simply of a funnel, in the apex of which were situated the pinhole and specimen, the latter held in place with aluminum washers. Cooling was accomplished by means of solid carbon dioxide and acetone. The open end of the funnel was fastened to a wooden frame which held a flat film. The collimator (not shown in the drawing) which defined the beam of x-rays, and which touched the camera, was constructed of wood to prevent the condensation of moisture upon it and to avoid the conduction of heat to the specimen.

In all x-ray investigations of rubber we have employed the copper K radiation from a Philips Metalix tube operating at 26 kv. and 22 ma.

Sodium chloride was used as a standard in the calibration of the cylindrical

camera. The distance from specimen to film was found to be 6.33 cm. Exposures for frozen rubber usually required from 5 to 10 hours.

Calibration of the low temperature flat-film camera was determined indirectly because of the difficulty in obtaining a reliable long-spacing standard. Previous work with sucrose in a calibrated camera had shown this material to be an unreliable standard for long spacings. At least the spacings do not agree with those of Becker and Rose.¹¹ We consider the cylindrical camera radius, as calibrated with sodium chloride, to be more reliable than the sucrose data. Hence, the sucrose spacings were calculated from the pattern obtained in the calibrated, cylindrical camera, the radii of the corresponding lines on the flat film were noted, and the distance from specimen to film of the flat-film camera was estimated to be 10.32 cm.

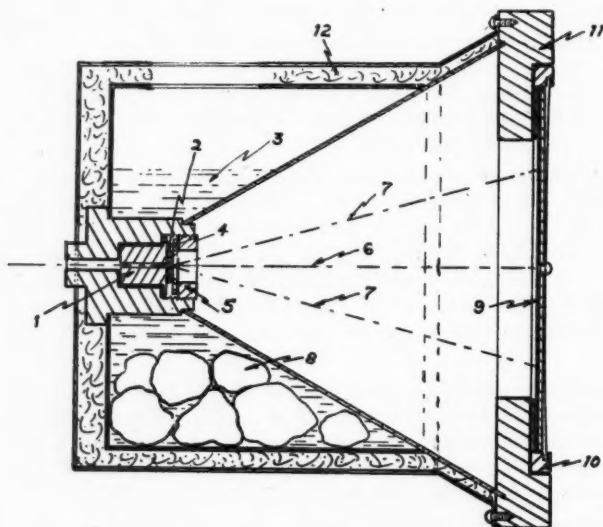


Figure 3—Low-Temperature X-ray Camera

- | | | |
|---------------------|----------------------|------------------|
| 1. Pinhole. | 5. Threaded washer. | 9. Film. |
| 2. Specimen. | 6. Undiffracted ray. | 10. Film holder. |
| 3. Acetone. | 7. Diffracted ray. | 11. Wood frame. |
| 4. Aluminum washer. | 8. Dry ice. | 12. Insulation. |

III. EXPERIMENTAL RESULTS

1. Behavior of Sol, Gel, and Total Rubber when Stretched

It is customary to consider the diffraction pattern which is obtained with stretched rubber as characteristic of the entire rubber hydrocarbon. This was found not to be the case when the sol and gel fractions which have been used in the present work were examined separately. The original observations were reported briefly by Clark, Warren, and Smith,¹² and since that report they have been confirmed.

When stretched, at room temperature, the purified total rubber hydrocarbon behaved exactly like any specimen of whole rubber, and produced a similar crystal fiber diffraction pattern.

The sol rubber fraction produced no evidence whatever of the characteristic crystal fiber pattern when stretched, even at 1000 per cent elongation. The liquid halo was retained at all elongations, but it became broader in proportion to the increased per-

centage of stretch. This may be caused by decreasing particle size. The same results were observed in the presence or absence of antioxidants.

When elongated 100 per cent or more, the gel fraction produced the characteristic crystal fiber pattern. At 200 per cent elongation the pattern was quite sharp and intense. The liquid halo remained unchanged in width but decreased in intensity as the crystal interferences increased in intensity. When, however, antioxidants were removed and the gel rubber was exposed to air for some time in the unvulcanized condition, it was difficult to find crystal interferences, even at 400 per cent elongation.

Samples of sol and gel rubber were vulcanized by the Peachey process. In this method, active sulfur is formed at room temperatures by the reaction between hydrogen sulfide and sulfur dioxide. Vulcanized sol rubber began to show faint evidence of crystal interferences when stretched more than 400 per cent, which showed that sulfur had produced a profound structural effect. Vulcanized gel rubber produced a fiber pattern, but not at elongations less than 250 per cent.

Differences in the physical properties of sol and gel rubber are indicated by their stress-strain behavior when vulcanized.¹³ The unvulcanized gel fraction, when milled, is the more difficult to "break down" or plasticize. The gel has much greater stiffness and more perfect elasticity; the sol is softer, more extensible, and when deformed takes a permanent set.¹⁴ The sol fraction is the more mobile of the two. For that reason, crystals which may be formed when sol rubber is stretched probably melt quickly and a diffraction pattern cannot be obtained. If successive strips of it were stretched, immediately before they were passed through an x-ray beam, evidence of crystallinity might be produced.

Pummerer¹⁵ separated total rubber into sol and gel by a modification of Feuchter's¹⁶ diffusion method, which differs from that used in the present study. Each of the fractions which he obtained produced a diffraction pattern when stretched. Subsequently, Hauser¹⁷ observed that rubber when extended very slowly, that is, isothermally, produced no interference.

2. Large Interplanar Spacing in Gel Rubber

When unstretched gel rubber is examined with the equipment for detecting and measuring the very long interplanar spacings, there appears a ring of small diameter with arcs which indicate fibering. (See Fig. 4.) It corresponds to a spacing of 54 A. U., or a multiple of this value, instead of 58 A. U., previously reported.¹⁸ When gel rubber is stretched, these arcs condense into very sharp equatorial spots, corresponding to this periodicity. There is a lateral separation of molecules or crystallites of 54 A. U., or perhaps a multiple of it, which persists in stretched gel rubber with the fibering. An examination of sol rubber indicated that no such spacing was present. It was reinvestigated under conditions which were carefully controlled, but no evidence of large spacing interference was produced by the sol phase.

3. Diffraction Patterns of Stretched Gel Rubber

The gel rubber, when stretched nearly to the breaking point, produced an intense diffraction pattern which was sharper than that obtained with total rubber. The diffraction data are given in Tables I and II. In these tables, and in those to follow, d is the distance between the set of planes, making an angle θ with the incident beam. R is radius of the diffraction spot or ring as measured on a flat film. L is the distance on the film from the diffraction line to the central spot when the cylindrical camera is used. When symbols are used to indicate relative intensities, they have the following conventional designations: s , strong; m , medium; w weak; and vw , very weak.

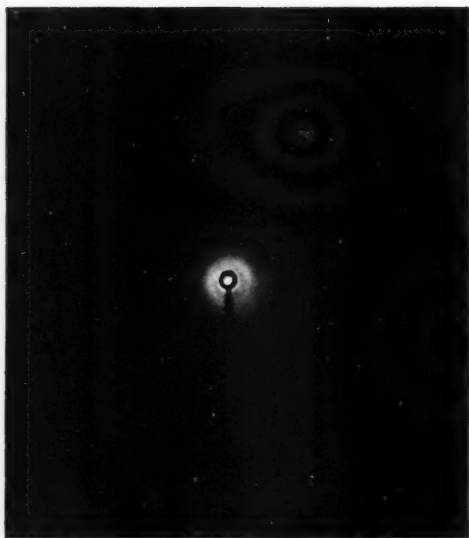


Figure 4—Long Spacing in Unstretched Gel
Room temperature. Exposure $18\frac{1}{2}$ hours.

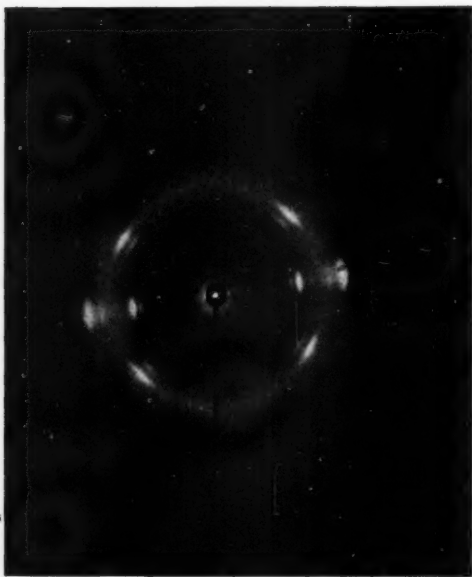


Figure 5—Pattern R57
Gel without sodium chloride. Stretched about 500 per cent. Fiber axis normal to beam. Room temperature. Exposure 6 hours.

TABLE I

X-RAY DIFFRACTION DATA FOR STRETCHED GEL RUBBER; SEE FIG. 5
Flat-Film Camera. Distance from Specimen to Film 5 Cm.

Pat- tern	R (cm.)	Equator		d	R (cm.)	First Layer Line		d	R (cm.)	Second Layer Line		d
		θ				θ				θ		
			A. U.					A. U.				A. U.
R57	1.26	7°	4.34'	6.24	1.98	10° 48.1'	...	4.102
	1.925	10°	31.41'	4.21
R61	1.258	7°	3.68'	6.253	1.60	8° 52.34'	...	4.983	2.435	12° 59'	...	3.421
	1.925	10°	31.7'	4.207	2.20	11° 52.5'	...	3.735
	2.738	14°	21.17'	3.100	2.44	13° 0.4'	...	3.41
R62	1.26	7°	4.33'	6.243	1.62	8° 58.56'	...	4.926	1.99	10° 51.1'	...	4.082
	1.94	10°	36.19'	4.177	2.215	11° 56.8'	...	3.714	2.477
	2.755	14°	25.64'	3.084	2.44	13° 0.375'	...	3.412

TABLE II

X-RAY DIFFRACTION DATA FOR STRETCHED GEL RUBBER; SEE FIG. 6
Flat-Film Camera. Distance from Specimen to Film 5.09 Cm. Pattern R64
(with NaCl)

R (cm.)	Equator		d	R (cm.)	First Layer Line		d	R (cm.)	Second Layer Line		d
	θ				θ				θ		
			A. U.				A. U.				A. U.
1.27	7°	0.3'	6.30	0.87	4° 51'	...	9.09	2.00	10° 44'	...	4.13
1.95	10°	29'	4.23	1.63	8° 53'	...	4.98	2.46	12° 54'	...	3.45
2.76	14°	14'	3.13	2.22	11° 47'	...	3.76
				2.47	12° 57'	...	3.43

The data in Table II are assumed to be more reliable than the data in Table I, because the distance from specimen to film was more accurately determined in this

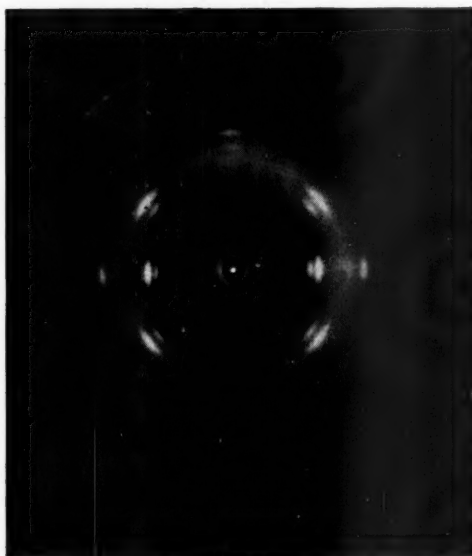


Figure 6—Pattern R64

Gel and sodium chloride. Stretched about 500 per cent.
Fiber axis 80° to beam. Room temperature. Exposure
16½ hours.

case by covering the sample with finely powdered sodium chloride. The results are in very good agreement with those of Lotmar and Meyer, as shown later in Table V. In view of the broad interferences in the pattern used by Lotmar and Meyer, it is surprising that the agreement is so good.

4. Diffraction Patterns of Frozen Sol, Gel, and Total Rubbers

In the present investigation, sol, gel, and total rubbers were examined individually, to compare the spacings and the intensities of interferences in their powder



Figure 7—Frozen Specimens

a, sol R29; b, R28; c, total R34. Cylindrical camera. Exposure 5 hours.

patterns, and also to compare the spacings of frozen rubber with those of stretched rubber at room temperature. Two types of patterns were taken of each kind of frozen rubber, one with the cylindrical camera and the other with the flat-film box camera. The data are recorded in Tables III and IV and the diffraction patterns

TABLE III

X-RAY DIFFRACTION DATA FOR FROZEN SOL, GEL, AND TOTAL RUBBERS; SEE FIG. 7
Cylindrical Camera. Distance from Specimen to Film 6.33 Cm.

Sol—Pattern R29			Gel—Pattern R28			Total—Pattern R34		
<i>L</i> (cm.)	θ Degrees	<i>d</i> A. U.	<i>L</i> (cm.)	θ Degrees	<i>d</i> A. U.	<i>L</i> (cm.)	θ Degrees	<i>d</i> A. U.
1.44 β	6.52	6.12	1.42 β	6.43	6.20	1.43 β	6.47	6.16
1.58	s7.15	6.17	1.57	s7.11	6.21	1.57	s7.11	6.21
1.77	m8.01	5.52	1.76	7.97	5.54	1.76	7.97	5.54
1.97	s8.92	4.96	1.96	s8.87	4.99	1.96	s8.87	4.99
2.12 β	9.58	4.17	2.10 β	9.51	4.20	2.11 β	9.55	4.19
2.36	vs10.68	4.15	2.34	vs10.59	4.18	2.34	vs10.59	4.18
2.65	ms11.99	3.70	2.62	ms11.86	3.74	2.64	ms11.95	3.71
2.86	m12.95	3.43	2.82	m12.76	3.48	2.82	m12.76	3.48
3.21	mw14.53	3.07	3.26	mw14.76	3.02	3.28	mw14.85	3.00
3.56	w16.11	2.77	3.49	w15.80	2.82			
						3.67	vw16.61	2.69
3.86	w17.47	2.56	3.86	w17.47	2.56	3.91	mw17.70	2.53
4.16	vw18.83	2.38				4.36	m19.73	2.28
4.52	vw20.46	2.20	4.47	w20.23	2.22			
4.84	m21.91	2.06	4.81	m21.77	2.07	4.78	mw21.63	2.08
5.14	w23.27	1.95				5.09	w23.04	1.96
						5.48	w24.80	1.83

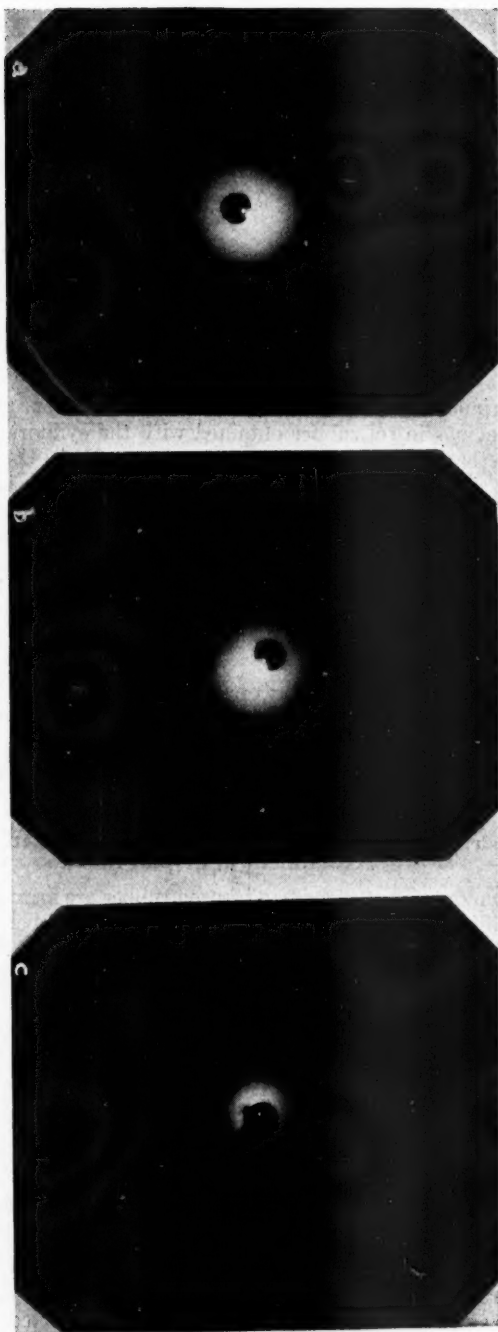


Figure 8—Frozen Specimens
a, sol R_{20} ; b, gel R_{22} ; c, total, R_{24} . Flat-film camera. Exposures 8 to 11 hours.

reproduced in Figs. 7 and 8. Uncertain interferences were not measured, as indicated by blank spaces in Table III.

TABLE IV

X-RAY DIFFRACTION DATA FOR FROZEN SOL, GEL, AND TOTAL RUBBERS; SEE FIG. 8
Flat-Film Camera. Distance from Specimen to Film 10.32 Cm.

Sol—Pattern R20			Gel—Pattern R22			Total—Pattern R24		
<i>R</i> (cm.)	θ	<i>d</i> A. U.	<i>R</i> (cm.)	θ	<i>d</i> A. U.	<i>R</i> (cm.)	θ	<i>d</i> A. U.
2.36 β	6° 26'	6.19	2.38	6° 30'	6.13	2.36	6° 26'	6.19
2.63	7° 9'	6.18	2.65	7° 12'	6.13	2.63	7° 9'	6.18
2.98	8° 3'	5.49	2.99	8° 5'	5.47	2.97	8° 2'	5.50
3.32	8° 55'	4.96	3.34	8° 58'	4.94	3.32	8° 55'	4.96
3.61 β	9° 38'	4.15	3.64	9° 43'	4.12	3.62	9° 40'	4.14
3.85	10° 14'	4.33	3.88	10° 18'	4.30	3.86	10° 15'	4.32
4.05	10° 43'	4.14	4.08	10° 47'	4.11	4.06	10° 44'	4.13
4.59	11° 59'	3.70	4.62	12° 4'	3.68	4.59	11° 59'	3.70

Within experimental error, the sol, gel, and total rubbers produce similar patterns. The spacings in sol rubber obtained with the cylindrical camera are uniformly smaller than the others by approximately 0.04 A. U., but the difference probably is not significant. The flat-film camera shows the gel spacings to be uniformly smaller than the others, which may be a temperature effect, since no special precaution was taken to insure a constant temperature. Some interplanar spacings, including the important 020 interference of the frozen rubber, could not be distinguished in patterns R22, R29, and R34, but were satisfactorily resolved by the flat-film camera, which uses a longer distance from specimen to film.

An analysis of the (200) line with a microphotometer gives a slight indication of a doublet character.

For each type of rubber, in order to prove that the "powder" pattern of frozen rubber was characteristic of rubber, a pattern was also obtained after warming up to room temperature. In all cases the crystal interferences disappeared completely, leaving only the halos obtained from ordinary unstretched rubber. These patterns are shown in Fig. 9.

5. Comparison between Stretched Rubber and Frozen Rubber, and the Assignment of Crystal Indices

The diffraction data on stretched and frozen rubber are arranged for comparison in Table V. The assignment of indices is based on the rubber structure given by Lotmar and Meyer. Values of *d* have been calculated from their $\sin \theta/\lambda$ values for stretched rubber, and are also recorded in the table for comparison.

The lower value for the (002) spacing in frozen rubber, 6.18 instead of 6.30 in stretched rubber, is undoubtedly beyond experimental error, and represents a significant difference which may be an effect of temperature. However, stretched rubber cooled to the same temperature as frozen rubber displays no change in its normal (002) spacing. Except for small differences in the (002) and (200) spacings, the principal interferences of frozen and stretched rubber confirm the structure of Lotmar and Meyer. Likewise the intensities compare favorably.

6. Sol and Gel Rubber Crystallized from Solutions

In earlier papers¹⁹ to which reference has been made, crystals of sol and gel rubber which were produced from solutions of these fractions were shown to be fine needles. They were birefringent between crossed nicols, an indication of crystallinity in some system other than cubic. Their melting behavior was reported, their analysis con-

TABLE V

SUMMARY OF INTERPLANAR SPACINGS (d , IN A. U.) FOR STRETCHED AND FROZEN RUBBER

Inten- sity	Lotmar and Meyer		Intensity	Pattern $R\theta$ (Stretched)	Present Investigation Frozen Rubber			Flat-Film Camera		
	Indices hkl	Stretched Rubber			Sol	Gel	Total	Sol	Gel	Total
<i>s</i>	002	6.29	<i>s</i>	6.30	6.17	6.21	6.21	6.18	6.14	6.18
<i>vw</i>	111	5.50	<i>mw</i>	..	5.52	5.54	5.54	5.49	5.47	5.50
<i>s</i>	012	5.00	<i>s</i>	4.98	4.96	4.99	4.99	4.96	4.94	4.96
<i>vs</i>	200	4.24	<i>vs</i>	4.23	4.15	4.18	4.18	4.33	4.30	4.32
<i>m</i>	020	4.10	..	4.13	4.14	4.11	4.13
<i>ms</i>	{ 210 013 211 }	3.76	<i>ms</i>	3.77	3.70	3.74	3.71	3.70	3.68	3.70
	{ 120 121 211 }	3.70
	{ 121 022 212 }	3.45	<i>m</i>	{ 3.45 3.43 }	3.43	3.48	3.48
<i>w</i>	004	3.14	<i>mw</i>	3.13
<i>w</i>	{ 220 023 221 }	3.01	3.07	3.02	3.00
	{ 114 221 222 }	2.86	2.82
<i>w</i>	{ 222 312 311 214 130 131 }	2.78	<i>w</i>	..	2.77	..	2.69
<i>vw</i>	{ 222 124 }	2.56	2.56	2.56	2.53
	{ 230 231 }	2.39	<i>vw</i>	..	2.38
<i>vw</i>	230	2.29
<i>vw</i>	304	2.23	2.20	2.22
<i>vw</i>	224	2.20	<i>vw</i>
<i>w</i>	224	2.08	<i>mw</i>
<i>vw</i>	034	2.06	2.06	2.07	2.08
<i>vw</i>	{ 421 420 }	1.92	<i>w</i>	..	1.95	..	1.96
	<i>w</i>	1.83

formed to the composition C_6H_8 , and their refractive index was the same as that of uncrystallized rubber at the same temperature. They have now been investigated by x-rays to confirm their crystalline character.

The rubber was deposited on a Cellophane disc about 2 cm. in diameter, the upper surface of which was roughened with sandpaper to hold the deposit in place. The discs had been extracted previously with hot water and with hot alcohol to remove plasticizing agents. Crystals formed slowly from dilute solutions during 2 or 3 weeks at temperatures between -38° and -48° C. In this range of temperature the velocity of crystallization is suitably repressed. The deposit was washed once with ether at -60° C., and transferred to cold 95 per cent ethyl alcohol, in which it was shipped from the National Bureau of Standards to the University of Illinois, surrounded by solid carbon dioxide. At low temperatures the fluidity of ethyl alcohol is quite low, so that there was little splashing and the deposit usually adhered to the disc. At the University of Illinois, the specimen was kept cold by suspending over liquid air in a vacuum flask until the x-ray exposure could be made.

The flat-film camera maintained specimens at temperatures between -20° and -40° C. during exposure. The camera, pinhole, specimen holders, and forceps were cooled by solid carbon dioxide and acetone. With the cooled forceps the specimen was transferred to a piece of porous plate placed upon solid carbon dioxide, and much of the alcohol was removed. Sometimes, especially in the early trials, the

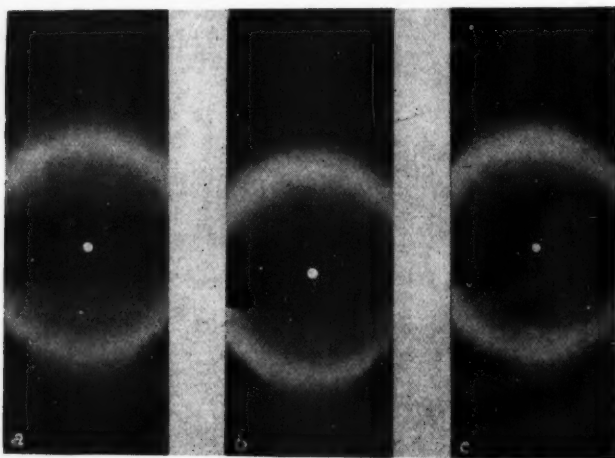


Figure 9—Specimens at Room Temperature
a, sol *R33*; b, gel *R32*; c, total *R36*. Cylindrical camera. Exposure 5 hours.

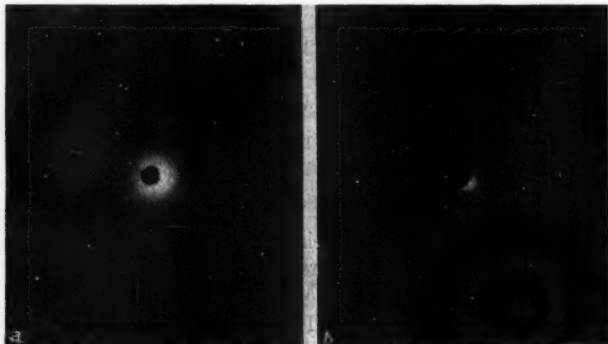


Figure 10—Gel Rubber Crystallized from Solution
a, *R38*, exposure 11 hours; b, *R39*, exposure $14\frac{1}{2}$ hours.

specimen was also covered by a celluloid disc. In the final experiments, no disc was used, and the specimen was simply spread over the pinhole. This had a diameter of 0.01 cm. The camera was properly aligned with the x-ray tube to give a beam of maximum intensity before the film was inserted. The exposures required about 10 hours.

After considerable experimentation with crystalline sol a diffraction pattern was finally obtained which was reproduced several times and which definitely showed

faint crystalline interferences, not suitable for accurate measurement and analysis, but confirming the crystalline nature of the specimen. The crystalline material is sometimes more compact than at other times. With the crystalline gel, powder patterns were obtained with specimens *R38* and *R39*, which are reproduced in Fig. 10. Many trials were made before the proper conditions were established. It is hardly necessary to emphasize the extraordinary experimental difficulties involved in work of this kind.

When the data in Table VI are compared with those obtained with frozen rubber, an excellent agreement is found for the three strongest interferences. There is no doubt therefore that the material is truly crystalline, and that the structures of the crystals are identical with those of crystals which form in massive, frozen rubber.

TABLE VI
X-RAY DIFFRACTION DATA ON CRYSTALLIZED GEL RUBBER; SEE FIG. 10
Distance from Specimen to Film 10.32 Cm.

<i>R</i> (cm.)	<i>R38</i> θ	<i>d</i> A. U.	<i>R</i> (cm.)	<i>R39</i> θ	<i>d</i> A. U.
2.65	7° 12'	6.14	2.62	7° 7.5'	6.19
3.33	8° 56.5'	4.95	3.31	8° 53.5'	4.97
4.06	10° 44'	4.13	4.04	10° 41.5'	4.14

IV. SUMMARY

Sol, gel, and total rubber were prepared by a method which avoided the effects of light and oxygen. The total rubber when stretched and exposed to an x-ray beam behaved like other specimens, and produced the characteristic crystal fiber pattern. Stretched sol rubber produced no evidence whatever of this pattern, even at 1000 per cent elongation. With stretched gel rubber, the pattern was formed above 100 per cent elongation and at 200 per cent was sharp and intense. The measurements of interplanar spacings agree excellently with the results reported recently by Lotmar and Meyer.

A large, interplanar spacing of 54 A. U. was found in the unstretched gel. It was absent in the sol.

Specimens of frozen sol, gel, and total rubber were examined with a cylindrical and with a flat-film camera to compare the spacings and intensities with those of stretched gel. Within experimental error, sol, gel, and total rubber produce similar patterns. The spacings are similar to those in stretched rubber, with the exception of the (002) spacing in frozen rubber, which is 6.18 A. U. instead of 6.30 A. U., the value in stretched rubber.

The pattern of gel, crystallized from solution, is similar to the patterns of stretched and frozen rubber.

We appreciate the coöperation of L. G. Polhamus, Bureau of Plant Industry, U. S. Department of Agriculture, who supplied latex of authentic origin.

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Enhanced Polymerization and Depolymerization of Natural Rubber by Quinones and Related Compounds¹

D. Spence and John D. Ferry

Introduction

Oxidizing Agents in Polymerization.—Oxygen and oxidizing agents play a rather puzzling dual role in the chemistry of polyprene substances. Under certain conditions, they cause breakdown and depolymerization of unsaturated hydrocarbon macromolecules. Purified natural rubber, for example, is very susceptible to attack by molecular oxygen, and the absorption of relatively small proportions is sufficient to form a sticky product which lacks tensile strength and dissolves readily in solvents to form solutions of low viscosity.² The action of a variety of oxidizing agents, such as potassium permanganate, hydrogen peroxide, and benzoyl peroxide, is similar.³ On the other hand, the opposite effect, namely, enhanced polymerization by oxidizing agents, has been observed. Thus, a vulcanization of rubber has been effected by benzoyl peroxide and nitrobenzenes,⁴ and the authors⁵ have successfully employed metallic compounds, such as potassium ferricyanide, to produce enhanced polymerization. Furthermore, in the kinetics of polymerization of dienes and other unsaturated compounds, oxygen⁶ and peroxides⁷ play important roles, and oxidizing agents are employed as catalysts for such polymerization reactions.⁸

The present paper is a study of the conditions which determine depolymerization or, alternatively, enhanced polymerization. It describes the treatment of natural rubber, in the form of latex and in benzene solution, with several oxidizing agents. Of these, the most completely studied is *p*-benzoquinone; in addition, the action of other quinones, other carbonyl compounds, and other quinonoid oxidants has been investigated. It has been found that enhanced polymerization or depolymerization can be achieved with small proportions of these reagents, depending on the experimental conditions. The results are interpreted in terms of concurrent reactions.

Terminology.—Natural rubber dissolves only partially in such solvents as benzene or ether, leaving a highly swollen residue which disperses extremely slowly, if at all.⁹ Although the terms "sol" and "gel" have been used to designate the soluble and insoluble fractions, respectively, some authors¹⁰ have preferred to consider the proportion of soluble to insoluble rubber simply as related to the average degree of polymerization of the material, which may contain fractions of a wide variety of molecular weights rather than two distinct components. In contrast to raw rubber, vulcanized rubber is practically insoluble; in rubber solvents it forms a swollen gel without appreciable solution into the solvent phase.

The term *polymerization* is here employed in its broader sense¹¹ to include the existence of cross-links between different macromolecules as well as links between the primary units in a straight-chain macromolecule. *Degree of polymerization*, in this respect, may be considered as a measure of the total number of links per unit volume of material; and "enhanced polymerization" and "depolymerization"

as creation or destruction, respectively, of such links.¹² Enhanced polymerization of a rubber-like material results in decreased solubility and decreased swelling of the insoluble residue "gel" and in increased tensile strength; depolymerization, the reverse. In vulcanized rubber, for example, the maximum tensile strength occurs at the same degree of vulcanization as the minimum swelling in solvents.¹³ Vulcanization may be considered as an enhanced polymerization without specifying whether the latter is "linear" (increase in length of chain molecules) or "random" (cross-linking) or both.

Experimental

Materials.—The material used in most of the experiments was *Hevea* latex buffered at p_H 6.8–7.1 with dilute phosphate buffers. An ammonia-preserved, centrifuged latex concentrate was furnished through the kindness of The B. F. Goodrich Company. It was purified by dialysis against 0.05 *M* phosphate buffer and subsequently sterilized according to the procedure of Spence and van Niel.¹⁴

The quinones, aldehydes, and ketones employed were Eastman products, used without further purification. Benzoquinone diimide and benzoquinone dichlorodiimide were prepared by oxidation of *p*-phenylenediamine (Eastman), according to the procedures of Willstätter and Mayer.¹⁵ The "oxidized quinone" was prepared by bubbling air through a slightly alkaline solution of hydroquinone, evaporating the solution to dryness, and heating the mass at 100° to volatilize any remaining hydroquinone and quinone. The involatile, dark brown residue dispersed in water readily.

Treatment of Latex and Removal of Oxygen Therefrom.—In order to heat or irradiate latex with reagents in the absence of oxygen, the latex was freed of air by bubbling through it nitrogen previously passed through alkaline pyrogallol solution. The Pyrex container was finally pumped off to about 20 mm. pressure and sealed. Irradiated samples were suitably agitated during exposure.

Preparation and Testing of Samples.—After treatment of the latex with the various reagents as described below, samples were coagulated either by adjusting the p_H to 4.8 with 10% acetic acid or by pouring the latex on tiles of unglazed porcelain.¹⁶ The rubber was extracted twice with cold acetone and dried *in vacuo* in the dark. A measure of the degree of polymerization was obtained by determining the solubility and degree of swelling.¹⁷ A portion of rubber was immersed in a volume of benzene (cc.) 100 times its weight (g.). After three days, the solution was decanted from the swollen gel and replaced by its own volume of pure benzene. After fourteen days, this process was repeated. The swelling of the residual gel was expressed by the "swelling index"—the volume of gel (cc.) divided by the weight of rubber in it (g.). All operations were conducted in the dark room.

Enhanced Polymerization and Depolymerization with Benzoquinone

Dark Reaction with Benzoquinone.—When benzoquinone is heated in aqueous solution in the absence of air, simultaneous reduction and oxidation occur, with the formation of hydroquinone and a dark brown oxidation product of complex composition.¹⁸ When rubber latex is heated with benzoquinone in solution, a similar reaction apparently occurs, but in addition a substantial enhanced polymerization of the rubber takes place in the absence of air.

Samples of latex of 5% rubber content were heated with *p*-benzoquinone, hydroquinone, and "oxidized quinone" in the absence of air. Data on the resulting rubbers (Table I) show that the hydroquinone and "oxidized quinone" are ineffective in the enhanced polymerization, which must then be due to the quinone itself or an intermediate product in its decomposition.

TABLE I

Latex, 5% Rubber Content; p_H 7.0 Heated for Five Hours at 100° in Nitrogen: Concentration of Reagents 0.25%

Rubber from	Proportion Soluble in 14 Days	Swelling Index
Untreated control latex	0.66	100
Quinone treated latex	0.31	38
Hydroquinone treated latex	0.74	80
"Oxidized quinone" treated latex	0.72	110

When neutral latex was allowed to stand at room temperature (in the dark) for fourteen days with quinone in solution, in the presence of air, the properties of the rubber remained unaltered.

Comparison of Light and Dark Reactions with Benzoquinone.—The simultaneous oxidation and reduction of quinone in aqueous solution, which occurs slowly at neutrality at room temperature, is greatly accelerated by irradiating with visible and ultraviolet light.¹⁹ Similarly, the enhanced polymerization of rubber in latex by quinone, which has not been detected at room temperature in the dark, is readily effected by irradiation. The results of the reaction in the dark and in diffuse daylight (Pyrex containers) are compared in Table II.

TABLE II

Treatment of Latex, 4% Rubber Content, p_H 6.2, Five Hours in the Dark and in Diffuse Daylight, with 0.2% Benzoquinone

Treatment			Proportion Soluble in 14 Days	Swelling Index
Untreated control		...	0.65	111
° C.				
90	Absence of air	Dark	0.35	23
90	In air	Dark	0.76	..*
20	Absence of air	Light	0.45	65
20	In air	Light	0.50	64
90	Absence of air	Light	0.17	22
90	In air	Light	0.78	..*

* Omitted because the amount of residual gel was too small.

At 90° presence of air causes depolymerization even in the light, and in every case the degree of enhanced polymerization achieved is better when air is excluded. The greatest polymerization occurs at 90° in the light, owing probably to the combined effect of light and dark reactions.

In general, the dark reaction (at elevated temperatures) involves the formation of relatively large amounts of "oxidized quinone," whereas in the reaction in light at room temperature a higher degree of enhanced polymerization may be achieved with very little formation of "oxidized quinone." The remaining experiments cited are devoted to the reaction in light.

Pre-irradiation of Quinone.—In order to show that the enhanced polymerization in the light is a photochemical process and not caused by a stable product of the irradiation of quinone, portions of latex and quinone solution were irradiated separately and mixed in the dark. The results (Table III) show that no enhanced polymerization is caused by this treatment or by irradiation of the latex alone.

Inhibitors and Light Filters.—It was found (Table IV) that the photochemical polymerization was not inhibited by a twofold excess of hydroquinone. The degree of enhanced polymerization was greatly diminished by an excess of "oxidized quinone," but this was probably the result of absorption of the actinic light as

TABLE III

Latex, Irradiated for Five Hours in Sunlight

Conditions	Proportion Soluble in 14 Days	Swelling Index
Non-irradiated control	0.62	100
Quinone solution and latex, irradiated separately and mixed in dark, standing 16 hours	0.62	92
Latex irradiated alone	0.69	97
Latex and quinone irradiated together	0.18	33

the same effect was produced by filtering the light through an aqueous solution of this substance.

TABLE IV

Latex, 10% Rubber Content, Irradiated in Sunlight for Six Hours with 0.1% Benzoquinone

Conditions	Proportion Soluble in 14 Days	Swelling Index
Non-irradiated control	0.33	100
No additional reagent (irradiated)	0.10	30
0.2% Hydroquinone added (irradiated)	0.10	27
0.2% "Oxidized quinone" added (irradiated)	0.28	71
Light filter of "oxidized quinone" (irradiated)	0.30	69

Enhanced Polymerization in Solid Rubber.—A film of rubber about 1 mm. thick, prepared by coagulation of latex and subsequent acetone extraction, was dried *in vacuo* and then exposed to the vapor of quinone in the dark at room temperature. After it had absorbed about 1% of its weight of quinone, it was placed in the sunlight for two hours. Pieces of commercial "first latex crepe," 1 mm. thick, were treated similarly, one being irradiated dry and the other immersed in water. In each case (Table V), enhanced polymerization occurred, showing the aqueous phase of the latex to be non-essential in this process.

TABLE V

Photopolymerization by Quinone in Dry Rubber

Material	Treatment	Proportion Soluble in 14 Days	Swelling Index
Latex film	Exposed to quinone vapor but not to light	0.46	107
	Exposed to quinone vapor and irradiated	0.12	14
Crepe	Non-irradiated control	Practically complete solution	
	Exposed to quinone vapor, irradiated dry	0.26	32
	Exposed to quinone vapor, irradiated in water	0.26	30

Irradiation of Rubber Dissolved or Swollen in Benzene.—In contrast with the results in latex or dry rubber, irradiation of benzene solutions of rubber (or benzene-swollen residual gels) with quinone in the presence of air at room temperature leads to marked depolymerization, as evidenced by a rapid fall of viscosity, and dissolution of gel structure. Even the product of enhanced polymerization by quinone, which swells in benzene without dissolving, can be disintegrated rapidly in the swollen state by irradiation with additional quinone provided air is present. The resulting solution has a viscosity differing little from that of the solvent, showing that the macromolecules have undergone marked breakdown. In the absence of light, however, quinone has no effect on the swollen gel rubber.

TABLE VI

Latex Irradiated with Various Quinones

Rubber Content	Time of Irradiation, Hr.	Quinone	Concentration, %	In Air		In Absence of Air	
				Proportion Soluble in 14 Days	Swelling Index	Proportion Soluble in 14 days	Swelling Index
Non-irradiated control				0.39	110	0.39	110
15%	3.5	Benzoquinone	0.07	0.18	28
		1,4-Naphthoquinone	0.11	0.04	10
		Chloranil	0.17	0.25	32
		Anthraquinone	0.15	0.61	108	0.08	24
10%	2	Benzoquinone	0.08	0.11	36
		1,4-Naphthoquinone	0.115	0	15
		Anthraquinone	0.155	0.12	29
10%	3	1,4-Naphthoquinone	0.12	0.18	15	0.11	18
		1,2-Naphthoquinone	0.12	0.24	32	0.20	28
		Tolu- <i>p</i> -quinone	0.09	0.20	34	0.33	46
		Phenanthrenequinone	0.16	0.51	57	0.14	19

* Chosen for equal molecular concentration in comparative experiments.

To show the dependence of the net result of photochemical treatment with quinone upon the degree of swelling (*i. e.*, the dilution) of the rubber, a thin sheet of

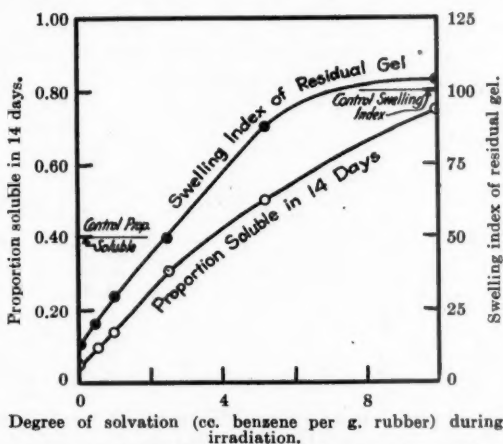


Figure 1—Rubber Irradiated with Benzoquinone while Swollen with Benzene to Different Extents: Samples Desiccated after Irradiation and Then Reimmersed in Benzene for Solubility and Swelling Measurements. Proportions of the Final Products Soluble in Fourteen Days, and Swelling Indices of the Residual Gels, Plotted against the Degree of Solvation during Irradiation

solid rubber was instilled with quinone vapor in the dark as described above. Pieces swollen in benzene to different extents were then irradiated. The resulting systems (partly swollen, partly dissolved) were freed from benzene by desiccation in the dark at room temperature, and the customary swelling and solution determinations were made on the dried products. The results (Fig. 1) grade uniformly from marked enhanced polymerization for irradiation in the absence of solvent to extensive depolymerization for irradiation of the rubber swollen in a tenfold excess of solvent.

Irradiation of rubber in the swollen state with quinone produced depolymerization even when the air was previously removed from the system by evacuation.

This does not, however, exclude the possibility that small traces of molecular oxygen are required for the breakdown process.

When a benzene solution of rubber to which quinone has been added is frozen and irradiated at -80° , enhanced polymerization occurs. After exposure of the solid solution for an hour to the sunlight (through a bath of alcohol cooled by solid carbon dioxide), warming to room temperature yields not the original solution but a firm gel. This gelatin is not produced by the freezing and melting alone or by irradiation of the solid solution without quinone.

Enhanced Polymerization and Depolymerization with Other Quinones

Comparative Results.—Irradiation of latex with a variety of quinones shows (Table VI) that, as in the case of benzoquinone, enhanced polymerization is produced (even in the presence of air) by tolu-*p*-quinone, chloranil, 1,2-naphthoquinone, and 1,4-naphthoquinone. Two other quinones, anthraquinone and phenanthrenequinone, produce, however, depolymerization in the air, but enhanced polymerization in the absence of air.

Dependence of Enhanced Polymerization upon Concentration and Time.—1,4-Naphthoquinone, as the most effective reagent in enhanced polymerization, was employed to show the effect of concentration and time on the reaction in latex (Table VII). Increase in the quantity of quinone above a small minimum concentration appears to have no effect, nor does prolonged exposure. The minimum concentration for maximum polymerization is for naphthoquinone about 0.4% of the rubber or 1 molecule per 600 isoprene units.

TABLE VII
Latex Irradiated with 1,4-Naphthoquinone

Rubber Content %	Concentration Naphthoquinone %	Time of Irradiation Hr.	Proportion Soluble in 14 Days	Swelling Index
Non-irradiated control		..	0.36	100
20	0.04	4	0.08	17
20	0.08	4	0.06	16
20	0.15	4	0.06	13
16	0.17	2	0.07	13
16	0.17	2.5	0.06	12
16	0.17	3	0.06	11
10	0.50	25	0.05	10

Enhanced Polymerization and Depolymerization with Other Carbonyl Compounds

Experiments with benzophenone and benzaldehyde showed that the former resembles the majority of the quinones studied, in effecting enhanced polymerization in latex through irradiation even in the air; the latter, like anthraquinone and phenanthrenequinone, produces breakdown in air but enhanced polymerization in its absence (Table VIII). Benzophenone, like benzoquinone, causes photodepolymerization of benzene-swollen rubber.

TABLE VIII
Latex, 15% Rubber Content, Irradiated in Sunlight with Benzophenone and Benzaldehyde

Reagent	Concn., %	Irradiation	Proportion Soluble in 14 Days	Swelling Index
Non-irradiated control	0.39	111
Benzophenone	0.27	3 hrs. in air	0.21	19
Benzaldehyde	0.75	3 hrs. in air	Practically complete	solution
Benzaldehyde	0.75	3 hrs. in N_2	0.01	9

Enhanced Polymerization with Other Quinonoid Compounds

To show that the oxygen and the carbonyl group in the polymerizing agents described above are not essential to the reaction, latex was treated with quinone diimide and quinone dichlorodiimide (Table IX). The former compound decomposed so rapidly with formation of a black pigment (Bandrowski's base,¹⁵ the analog of the "oxidized quinone" from benzoquinone) that irradiation was not effective. However, polymerization was produced by heating in the absence of air. The dichlorodiimide caused marked enhanced polymerization both by heating and by irradiation.

TABLE IX

Latex, 5% Rubber Content, with 0.25% Quinone Imides

Imide	Treatment	Proportion Soluble in 14 Days	Swelling Index
Untreated control		0.39	111
Quinone diimide	Heated in absence of air 4½ hrs.	0.24	53
Quinone dichlorodiimide	Heated in absence of air 5 hrs.	0	7
	Irradiated in air 4 hrs.	0.05	13
	Irradiated in absence of air 4 hrs.	0	8

Nature of the Reactions

The results are consistent with the course of two concurrent reactions between the rubber and the polymerizing agent, one leading to enhanced polymerization and the other to depolymerization. The latter process is in every case favored by (a) decreasing the rubber concentration in the reaction system, (b) increasing the temperature, (c) the presence of molecular oxygen.

A decrease in the rubber concentration is occasioned by presence of a solvent or swelling agent. Latex of any dilution, the rubber particles being on the average about 1 μ in diameter, may be considered as rubber in the undiluted solid phase. The only difference in behavior between solid rubber and latex, in the reactions here discussed, is in accessibility to actinic light. In a thick layer of solid rubber, a large part of the light is absorbed near the surface, shielding the interior, while in latex the individual particles can be brought in turn to the periphery of the vessel and receive irradiation of full intensity. Agitation or circulation of the latex facilitates this result.

The effect of actual dilution of the rubber phase, by a solvent or swelling agent, indicates that the enhanced polymerization process is of higher order than the depolymerization process. The influence of temperature is shown by the enhanced polymerization produced even in dissolved rubber when the solution is illuminated at -80° , as well as by the rapid breakdown of latex in air which occurs at 90° with any of the reagents described. It appears that some step in the depolymerization process involves an activation energy which is high compared with those concerned in the enhanced polymerization. Finally, the influence of molecular oxygen indicates that its presence is necessary for the depolymerization.

Process of Enhanced Polymerization.—The primary photochemical process is not definitely known, but is probably absorption by the quinone, since purified rubber is transparent to light of wave lengths down to 2400 A. U.²⁰ The reaction has not yet been studied in monochromatic light, but is effected by the mercury arc as well as by sunlight. The high efficacy of 1,4-naphthoquinone in enhanced polymerization in the sunlight may be due to its greater absorption in the range of visible wave lengths. Ciamician and Silber²¹ described photochemical reactions of benzoquinone, benzophenone, and benzaldehyde with various alcohols. The alcohols were

dehydrogenated to aldehydes and ketones, while the light-activated compounds were reduced to hydroquinone, benzopinacolone, and hydrobenzoin, respectively. The reaction with rubber is probably similar, the dehydrogenation leading to the formation of new bonds between macromolecules, as suggested by van Rossem, *et al.*, for the vulcanization of rubber by benzoyl peroxide.²² The quinones are probably reduced to the corresponding hydroquinones and the quinone imides to *p*-phenylenediamine. It is possible that a portion of the reagent may remain in permanent combination with the rubber.

If such cross-linking bonds could be formed at any point along the rubber molecule, one would expect prolonged treatment with a large quantity of reagent to lead to a highly bridged type of three-dimensional polymer which would be hard and inextensible and would not swell at all in solvents. Actually the result of prolonged treatment is a product resembling soft vulcanized rubber, and the maximum amount of reagent effective is very small. This suggests that only the end of the macromolecule forms a complex with the photoactivated quinone or ketone which results in a new link with a second macromolecule. When all the ends have reacted, no amount of further treatment is effective. The mole ratio quoted above for naphthoquinone, 1 per 600 isoprene units, would lead on the above basis to a molecular weight for rubber of 80,000 which is of the order of magnitude suggested by determination of osmotic pressure,²³ viscosity,²⁴ sulfur addition,²⁵ and oxygen content.²⁶ It is possible, on the other hand, that the small number of reactive locations correspond to the active hydrogens found by Midgley, *et al.*,²⁵ in approximately the same proportion.

Process of Depolymerization.—It seems necessary to postulate another type of complex which a photoactivated quinone or ketone molecule can make at any point along the rubber chain, this complex being oxidizable by molecular oxygen with consequent rupture of the chain. This is supported by the fact that anthraquinone and phenanthrenequinone, which cause depolymerization when irradiated in latex at room temperature, have the lowest reduction potentials of the seven quinones studied, so that their complexes with the rubber molecule would probably be correspondingly more easily oxidized.

The simplest explanation for the predominance of depolymerization in benzene solution is probably that the dilution of the rubber by solvent permits frequent inactivation of terminal quinone complexes before links to neighboring macromolecules can be consummated.

Relationship to Sulfur Vulcanization

Study of the reactions involved in the vulcanization of rubber by sulfur is complicated by the addition of sulfur to the double bonds of the hydrocarbon. After a century of investigation, the relationship, if any, between the enhanced polymerization and this chemical combination of sulfur with the rubber has not been established.

Unpublished work by one of us has shown that when raw rubber is vulcanized in the presence of varying amounts of acetic acid, no enhancement of polymerization occurs if sufficient acid is present, although the rate of sulfur addition remains unchanged. An actual softening (depolymerization) may result by prolonged heating in the presence of acids at the temperature of vulcanization. Furthermore, the well-known improvement in physical properties brought about by the presence of small quantities of zinc oxide in vulcanization is not in fact accompanied by any increase in the amount of sulfur which has entered into combination with the rubber.²⁷ Vulcanizates containing very small proportions of total sulfur to rubber (0.2 to 0.5%), which may be prepared with certain types of ultra-accelerators, are as highly polym-

erized as those with high sulfur content.²⁸ Bruni has shown²⁹ that as little as 0.15% of sulfur is sufficient to give rubber the physical properties characteristic of vulcanization.

There is evidence that, in the total absence of accelerators (including those naturally occurring in raw rubber), the polymerization produced by sulfur is practically insignificant. This is known to be the case for certain synthetic rubbers³⁰ and for purified natural rubber.³¹ It is then possible that in sulfur vulcanization the actual enhanced polymerization is produced by dehydrogenating agents—analogueous in their action to those described in the present paper—which are formed by preliminary reactions between sulfur and the so-called "accelerators" present. Such a hypothesis would explain the action of the nitroso compounds³² as accelerators in vulcanization, and is supported by the fact that certain sulfur-containing "accelerators," such as thiuram disulfides—of a structure which might be expected to be effective in dehydrogenation—produce vulcanization in the absence of molecular sulfur.³³ It is hoped that future work may define more clearly the parallelism between oxygen and sulfur in these reactions.

The products of enhanced polymerization here described differ negligibly in chemical composition from natural raw rubber and are entirely free from sulfur. They may prove useful in cases where the presence of sulfur is objectionable in vulcanized rubber.

In both enhanced polymerization and depolymerization, the rubber is oxidized; in the one case presumably by dehydrogenation, and in the other with the introduction of oxygen. Further development of this distinction may offer a clue to the mystery of how the rubber is built up and subsequently broken down in the plant.

Summary

1. The enhanced polymerization or the depolymerization of natural rubber may be effected thermally or photochemically by one and the same reagent.
2. The action of quinones, carbonyl compounds, and other quinonoid compounds in this connection has been studied.
3. Depolymerization is favored by (a) dilution of the rubber by a solvent or swelling agent, (b) increase of temperature, (c) presence of molecular oxygen.
4. The results are interpreted in terms of concurrent reactions.

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- ¹ The results here recorded form the basis of U. S. Patent applications assigned to The B. F. Goodrich Company.
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- ¹⁴ Spence and van Niel, *Ind. Eng. Chem.*, **28**, 847 (1936).
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²⁷ Experimental data covering these observations will be published elsewhere along with matters of technical importance referred to in this communication.

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A Study of the Formation of Rubber in the Plant

Otto Ambros

The first chemical investigations of rubber can be traced back to 1860, when Williams decomposed rubber and succeeded in isolating isoprene. He advanced the idea that isoprene is an essential constituent of rubber, and this point of view was confirmed somewhat later by the researches of the French investigator Bouchardat.

Bouchardat observed that, when exposed to air, isoprene is transformed into a resinous substance, and he interpreted this phenomenon as a polymerization of the unsaturated hydrocarbon under the influence of atmospheric oxygen. This theory was confirmed at the beginning of the present century when Harries succeeded in identifying the pentadiene group in levulinic aldehyde obtained by the particular method which he used in decomposing the ozonide of rubber. Since then, the results of x-ray examination of rubber have lent support to the concept that rubber is an aggregation of thousands of long chains of unsaturated hydrocarbons formed from isoprene.

Physiological studies have not yet been able to explain in what manner the hydrocarbon isoprene is formed as a metabolism product in the plant cells, nor has the mechanism of the formation of latex been explained.

According to a somewhat prevalent idea, latex serves to protect the plant when it is wounded. The suggestion of Spence, in an article published in 1908, seems, however, more reasonable. According to Spence, rubber plays in the economy of the plant the part of a reserve substance analogous to starch. It is conceivable that a system of oxidizing enzymes splits rubber into intermediate products, which the plant can utilize whenever the need arises.

These ideas may be linked to the hypothesis of Harries, according to which rubber is formed at the expense of pentoses through the intermediate formation of isoprene. Whatever may be the answer to the problem, it is certain that, during the synthesis of rubber in the plant, isoprene is formed as an intermediate product. The question then arises as to the manner in which rubber is formed from isoprene.

The biological processes which take place in the plant at normal temperatures and under the ordinary biological conditions of the vegetable cell are popularly attributed to the action of some form of enzyme. However, no enzymes are known which bring about polymerization. On the other hand, it is a perfectly well known fact that in the case of dienes and their polymers, a slight impulse is all that is necessary to induce polymerization which, once started, turns into a very lively reaction because of its exothermic nature.

Nevertheless, under biological conditions, rubber is synthesized at a very slow rate, and it seems certain that some form of enzyme acts as a priming agent of polymerization.

With these facts in view, the theory is suggested that in the cells of the plant there exists, in the form of a milk, a finely divided system of the hydrocarbon which is to be polymerized. The plant has at its disposal very effective emulsifying agents, such, for example, as sterols. Because of this very fine dispersion, the action of the catalyst at the points of contact is facilitated in an ideal way. The

enzymatic catalytic action becomes operative when the catalase, present in each cell, liberates oxygen from the hydrogen peroxide formed in the respiratory process. Oxygen, aided by other oxidases, oxidizes a small quantity of hydrocarbon, thus develops energy in the cell, and thereby brings about polymerization of most of the isoprene.

In aqueous emulsion the hydrocarbon is too dilute to enter into the series of reactions involved in polymerization. Nevertheless, the cell is capable of furnishing all the compounds necessary to the reaction brought about by the enzymatic system, including both catalyst and oxidase, which, in the last analysis, govern polymerization.

To support this hypothesis, a series of experiments was carried out in a laboratory in Sumatra. The aim was to simulate the action of the cell as closely as possible, and to this end a neutral and stable emulsion of isoprene in water was first prepared with the aid of a suitable emulsifying agent. The milk-like emulsion at an average temperature of 28–30° C. was agitated violently in tightly stoppered bottles. To this emulsion small proportions of dilute hydrogen peroxide were added.

The rubber was determined by coagulation with alcohol and drying the precipitate to constant weight. The precision of the method was controlled by a duplicate series of experiments.

The first point to be verified was the action of the natural enzyme which supposedly is present in latex. To this end it was necessary to separate rubber from latex under conditions which would leave the enzyme unaltered in solution. A biochemical method was utilized for precipitating the rubber. To freshly gathered latex were added a few drops of a solution of papain. In this way a neutral serum free of rubber was obtained. In a control test rubber was precipitated by acetic acid and the serum was neutralized.

The first series of tests gave the following results:

Mixture	Composition of the Emulsion	Rubber Polymerized (Grams)
I	Isoprene in water	5.76
II	Mixture I + emulsifying agent + hydrogen peroxide	5.95
III	The same with neutral serum from the precipitation by papain	14.9
IV	The same with neutral serum from the precipitation by acetic acid	7.4

These weights show that the serum obtained by biochemical means has a very great influence on the polymerization.

With a view to determining the specific effect of enzymes, a series of tests was made with the same mixtures as described above, but for shorter times. The results follow:

Mixture	Composition of the Emulsion	Rubber Polymerized (Grams)
I	Isoprene in water	0.4
II	Mixture I + emulsifying agent + hydrogen peroxide	0.42
III	The same with serum from the precipitation by acetic acid and not neutralized	0.5
IV	The same with serum from the precipitation by acetic acid and neutralized	8.0
V	With neutral serum containing papain	10.2
VI	With neutral serum containing papain and also hydrocyanic acid	0.4
VII	Isoprene, water, emulsifying agent, serum containing papain; no hydrogen peroxide	0.0

After making these quantitative experiments, qualitative experiments were carried out to show the effect on the system of oxidizing ferments. In these experiments the latex was exposed in the open air. At the end of a few hours the color became deeper as a result of the concurrent action of the oxidizing ferments, except in the case of latex which was acidic and latex which had been poisoned with hydrocyanic acid.

Conclusions

The hypothesis is advanced that the natural polymerization of isoprene in plant cells is induced and accelerated by an oxidation which in turn is brought about through the agency of a system of enzymes.

Experiments in a laboratory in the tropics show that the serum of latex has an accelerating action on the polymerization of emulsions of isoprene in water containing hydrogen peroxide, and that this effect is nullified if the action of the enzymes is arrested by an acid or by a poison such as hydrocyanic acid.

Acknowledgment

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The Kinetics of the Coagulation of Latex of *Hevea Brasiliensis* and the Separation of the Hydratant Acid

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In the present work, an attempt is made to study the process of coagulation of *Hevea brasiliensis* latex, so familiar to every rubber expert, from a general colloid-chemical point of view, and to ascertain the physical conditions under which the kinetic phenomena take place.

Hevea Brasiliensis Latex as a Physical System

In "The Electrometric Determination of the Hydrogen Ion Concentration in the Latex of *Hevea brasiliensis* and Its Applicability to Technical Problems"¹ the true character of *Hevea brasiliensis* latex as a physical system and the phenomena which take place during coagulation of this system are discussed in the light of investigations and observations of various rubber experts.

Latex is a dispersion composed of polydispersed rubber hydrocarbon, serum components, and water. The rubber component consists of microscopically visible solid or semi-solid particles, in Brownian movement, and judged by the degree of affinity of rubber for water these particles are unquestionably lyophobic. Since the serum components are in a colloidal state, they are present as sols or emulsions, and they impart to the latex its lyophilic properties. It is possible, however, to choose the conditions of coagulation so that, for a given concentration of dispersed substances and at a given temperature, the dispersion will be predominantly lyophobic or lyophilic. This dual standard leads to the conclusion that *Hevea brasiliensis* latex is a pseudo-lyophilic dispersion. In saying this, it should be noted that, although the dispersion has several lyophilic properties, it is nevertheless essentially a lyophobic system, the properties of which become manifest under the right conditions.

In the coagulation of latex, it is to be observed that flocculation first occurs, and this is followed by gelation. Theoretically it must be assumed that an electric discharge and a dehydration are necessary to bring about flocculation, and as a result of this the dispersion loses its stability. Gel formation is the result of a swelling and rehydration of this flocculate.

The coagulation process in *Hevea brasiliensis* latex thus proceeds in two stages, though its progress can be interrupted in the first stage so that only floccules appear. In this case it is possible to bring about the second stage of coagulation of the flocculate to a gel artificially by a change in acidity or by the addition of hydrating substances. These latter substances may be designated as *hydratants*; they bring about the gelatinization of the floccules by absorbing water, either directly or indirectly.

Transformation of the floccules to a gel, which is the essential phenomenon in the production of rubber by coagulation, is called coalescence.² It has been proved

microscopically³ that hydratants bring about coalescence by virtue of their own absorption of water, and that they act as an agglutinant of the rubber particles.

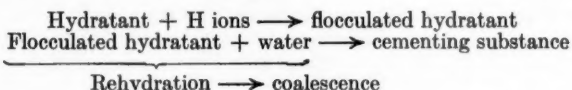
The Kinetics of Coalescence under Definite Conditions

If the process of coalescence can be explained as an agglutination of flocculated rubber particles brought about by the so-called hydratants, it should in turn be possible to explain the kinetics of coalescence in a simple manner, *viz.*, on the basis that coalescence depends solely on decomposition of the hydratant to an adhesive or cement-like substance, the function of which is probably to bind the flocculated rubber aggregates together. In this cementing action the lyophilic property of the hydratant predominates over the lyophobic property of the pure rubber dispersion, and the lyophilic character of latex is governed wholly by the presence of hydratants.

If a constant temperature is assumed, the same line of reasoning can be followed as in the derivation of the law of mass action and its application to molecular reactions.⁴ This is possible because of the fact that there is practically no change of temperature during the coagulation of rubber latex.

The particles of hydratant separate as floccules as a result of the acidity of the medium and in virtue of their absorption of water; they then swell to form a cement-like substance, which in turn brings about coagulation. For any given concentration of rubber and any given degree of acidity, coalescence is considered to take place at the moment when the free rubber floccules cohere to a compact gel. For this to occur, a similar quantity of cementing substance must be present under the particular conditions designated.

The problem of the rate of coalescence is therefore reduced to the question of how the quantity of adhesive substance formed in a given time varies both with the concentration of hydratant for a given concentration of latex and with the concentration of hydrogen ions. Schematically the formation of the cementing substance can be represented in the following way:



In these reactions one of the components (water) remains unaltered, and therefore the reactions are pseudo-monomolecular. If the concentration of hydratant is twice as great, the probability of formation of the cementing substance becomes twice as great; the formation of the latter also depends on the rate of flocculation of the hydratant. This rate of flocculation is a function of the acidity; however, the concentration of the hydratant will always be greater at the moment of coalescence than the concentration of cementing substance which is formed.

In the present discussion, rapid flocculation of the hydratant is assumed, so that the influence of slow flocculation on coalescence can be disregarded.

A further condition essential to the present line of reasoning is that the ratio of the quantity of hydratant and the concentration of rubber in the latex shall remain constant throughout any individual experiment. If any hydratant is formed during an experiment, the demonstration which follows is valid only if the ratio:

$$\frac{\text{hydratant}}{\text{concentration of latex}}$$

is at its maximum, or if the differential quotient of the two factors is very small or is equal to zero.

Under the conditions described above, the quotient of the increase in quantity of cementing substance and the increase in the time of coalescence is equivalent to the quantity of hydratant present:

$$\frac{dk}{dt} = K_1 (\text{concn. of hydratant} - \text{concn. of cementing substance})$$

If during an experiment the concentration of hydratant remains constant and is relatively great, but relatively small in comparison with the concentration of rubber hydrocarbon, then the concentration of cementing substance is very small at the moment of coalescence, so that:

$$\text{concn. of hydratant} - \text{concn. of cementing substance} = \text{concn. of hydratant}$$

The reaction equation then becomes:

$$\frac{dk_f}{dt} = K_1 C_h$$

where

dk_f = the increase in quantity of cementing substance, formed from the hydratant by rehydration in the time interval dt

$\frac{dk_f}{dt}$ = the rate of formation of cementing substance

= rate of coalescence

K_1 = a velocity constant

C_h = the concentration of hydratant in grams per 100 grams of dry rubber in the dispersion

Since under given conditions of concentration of latex, temperature, and acidity, the quantity of cementing substance necessary for coalescing the rubber component can be regarded as constant, and therefore since under these same conditions the criterion of coalescence is always a fixed point of measurement of a progressive process rather than an end-point, integration of the equation

$$\frac{dk_f}{dt} = K_1 C_h$$

between the limits t = time of coalescence and t_0 = initial time = 0 gives:

$$\int dk_f = \int_{t_0}^t K_1 C_h dt$$

The quantity of cementing substance formed is:

$$K_1 t C_h$$

Since the quantity of cementing substance, as explained above, is constant for a given set of experimental conditions, the product:

$$K_1 t C_h$$

also has a constant value. This can be expressed by the formula:

$$ht = K$$

in which h is the concentration of hydratant in grams per 100 grams of dry rubber, t is the time for coalescence, K is the coalescence constant (which depends on the concentration of latex, acidity, and temperature), and ht is the coalescence product.

The rate at which *Hevea brasiliensis* latex coagulates under a given set of conditions depends on the concentration of hydratant, and this factor plays a predomi-

nant part in the kinetics of coagulation. The coalescence of the rubber component progresses with time, so that at the first visible evidence of coalescence in the rubber dispersion (this period of time will by definition be designated as the *coalescence period*) the rate of coalescence is not equal to zero. Since the limiting case of the transformation of a loosely flocculated mass (flocculation) to a coherent gel (coalescence) has been assumed as a criterion of coagulation of Hevea latex, the time of coagulation, not the rate of coagulation, should be used hereafter as a characteristic and as a basis of comparison of coagulation processes. In practice, the concept of the technical time of coagulation may be retained for the actual coagulation process, in which case the formation of a clear serum, *i. e.*, complete precipitation of the colloids, represents the end-point.

A Study of the Kinetics of Coalescence Based on Experimental Results

In 1923 de Vries and Beumée-Nieuwland⁵ carried out an extensive investigation on coalescence by the inoculation of uncoagulated latex with fresh latex. When a natural hydratant was added to the flocculated dispersion of rubber, a gel formed after a certain interval of time. According to these authors, there were indications that the curves representing the time of gelling as a function of the quantity of fresh latex (hydratant) were not straight lines.

If this conclusion is studied more closely, it will be found that for the curves to be straight lines the following equation must hold true:

$$h = kt + C$$

where h is the quantity of hydratant, t is the time of coalescence, and k and C are constants, which are either positive or negative (C may also be zero). h and t are always positive, because it has been found by experiment that t increases as h diminishes, so that C must always be greater than $-kt$.

If the curves of de Vries and Beumée-Nieuwland are calculated by the formula above, it is found that the relation actually is not a straight-line function.

The problem therefore resolved itself into whether it is possible to express the experimental values as a $h:t$ function of the form:

$$t^{m^1} \times h^{n^1} = K_1$$

This is a polytropic curve, which can be represented in simplified form thus:

$$\sqrt[m^1]{t^{m^1} h^{n^1}} = \sqrt[m^1]{K_1} = K$$

whence

$$t = \frac{K}{\sqrt[n^1]{h^{n^1}}} = Kh^n$$

if

$$n = \frac{n^1}{m^1}$$

In the formula: $t = Kh^n$, t and h are variable; K and n are constants.

This formula can be expressed logarithmically thus:

$$\log t = \log K + n \log h$$

and with its aid it is possible to calculate whether the equation: $ht = K$, derived theoretically, shows any relationship with experimental measurements. The calculated logarithms were correlated with the results of de Vries and Beumée-Nieuwland, and additional experiments were also carried out to obtain as much

information as possible on the coalescence of Hevea latex under accurately controlled conditions at a constant temperature, with the use of buffer mixtures of the same hydrogen-ion concentration, with a constant concentration of rubber in the dispersions, with the exclusion of the effects of microorganisms or spontaneous fermentation, and with rapid flocculation of the hydratant.

In Fig. 1, the abscissa represents the logarithms of the quantities of inoculating liquid ($\log h$), and the ordinate the logarithms of the corresponding times for coalescence to occur ($\log t$) in twelve experiments. The numbers of the experiments are designated on the lines.

The directions of the lines in Fig. 1 are almost the same, while the points ($\log h : \log t$) for the same series of experiments lie in a straight line.⁶

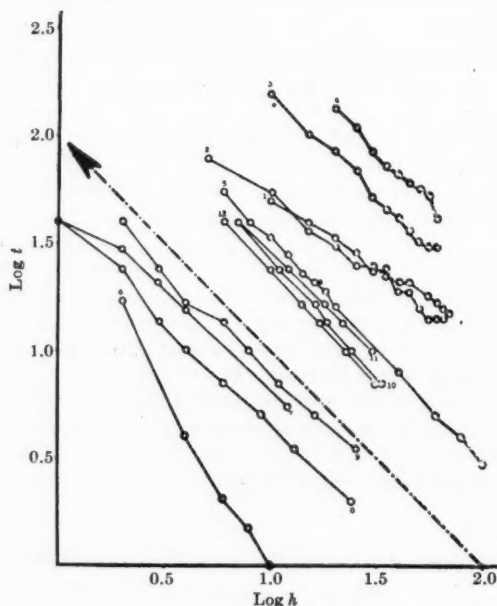


Figure 1

The lines run parallel with a line which can be drawn between the points: $\log h = 2$ and $\log t = 2$.

The exponent n in the equation

$$t = Kh^n$$

can be found from the differential of the function for the logarithm line

$$\log t = \log K + n \log h$$

from which

$$n = \frac{d \log t}{d \log h}$$

Figure 1 shows that

$$n = \frac{d \log t}{d \log h} = -1$$

The experiments show therefore that

$$t = Kh^{-1}$$

$$ht = K = K_2$$

and thus they confirm the truth of the theoretical deduction, *viz.*, that the coalescence product of Hevea latex has a constant value.

The analytical expression of this function is an equilateral hyperbola, whose axes h and t are the asymptotes ($xy = c^2$).

This holds true when the quantity of hydratant at the moment of coalescence is large compared with the quantity of cementing substance formed. When this is not true, and coalescence takes place only after a long time with small quantities of hydratant and a relatively large quantity of cementing substance formed from the latter, then the equation

$$\frac{dK_f}{dt} = K_1 C_h$$

is not true, but rather the equation

$$\frac{dk_f}{dt} = K_1(C_h - C_a)$$

which can be calculated approximately if C_a (the concentration of cementing substance) is determined with precision.

Under normal conditions of coagulation of Hevea latex, however, an excess of hydratant is always present, and at the moment of coalescence flocculated latex can always be inoculated with fresh serum from this coalescence.⁷

The Influence of Temperature on the Kinetics of Coalescence

Since coalescence may be regarded as a flocculation phenomenon with impacts of the rubber particles, according to the law of probability, and since agglutination of these particles depends wholly on the hydratant (which owes its agglutinating action to a molecular reaction), the influence of temperature changes on the kinetics of coalescence may also be considered to be a functional relation between temperature and rate of reaction.

The formula of Arrhenius⁸ is applicable to the representation of the rate of reaction as a function of the temperature. The rate increases rapidly with increase of temperature. The number of contacts of rubber particles remains about the same, but the percentage of favorable contacts, and consequently the likelihood of cohesion, increases.

The constant K_1 in the equation

$$\frac{dk_f}{dt} = K_1 C_h$$

changes with the temperature in accordance with the following law:

$$K_1 = Ae^{-\frac{E}{RT}}$$

where $e^{-\frac{E}{RT}}$ = $\frac{\text{number of contacts with great probability of cohesion}}{\text{total number of contacts}}$

R = molecular constant

T = the absolute temperature

E = the energy of activation, *i. e.*, the minimum energy with which contacts must occur

e = the basis of natural logarithms

When in a series of experiments the concentration of hydratant is maintained constant while the temperature changes:

$$\frac{dk_f}{dt} = (K_1)_T \times \text{constant} = A_1 e^{-\frac{E}{RT}} \text{ constant} \\ = A_1 e^{-\frac{E}{RT}}$$

The rate of coalescence is:

$$A_1 e^{-\frac{E}{RT}}$$

At a constant temperature the quantity of cementing substance for a constant concentration of hydratant is:

$$K_f = A_1 e^{-\frac{E}{RT}} t$$

and since with a constant concentration of hydratant the coalescence K_f attained, i. e., the quantity of cementing substance, is likewise constant, the time of coalescence as a function of temperature may be represented thus:

$$t = \frac{K_f}{A_1 e^{-\frac{E}{RT}}} = A_2 e^{\frac{E}{RT}}$$

This indicates that under otherwise constant conditions, the time for coalescence to take place diminishes with increase in temperature.

An investigation was then made of latex diluted to various extents to ascertain the influence of lowering the temperature on the time required for coalescence with a constant hydrogen-ion concentration. The ratio of the percentage of hydratant to dry rubber content was the same in all the experiments. When, however, the temperature was changed, the hydrogen-ion concentration also changed, and this effect had to be eliminated by interpolation.

To test the formula

$$t = A_2 e^{\frac{E}{RT}}$$

by the results obtained experimentally, Fig. 2 was constructed. Here the abscissa represents the logarithm of the time of coalescence and the ordinate the value $1/T$ in absolute degrees.

The following $1/T$ values were found to be for four different temperatures:

Temperature (Celsius)	Reciprocal Values (Absolute Degrees)
9	0.00355
13	0.00350
18	0.00344
21	0.00340

$$\log t = \log A_2 + \frac{1}{T} \times \frac{E}{R} \log e$$

$$\frac{d \log t}{d\left(\frac{1}{T}\right)} = \frac{E}{R} \log e = E \frac{\log e}{R}$$

From Fig. 2, it is evident that:

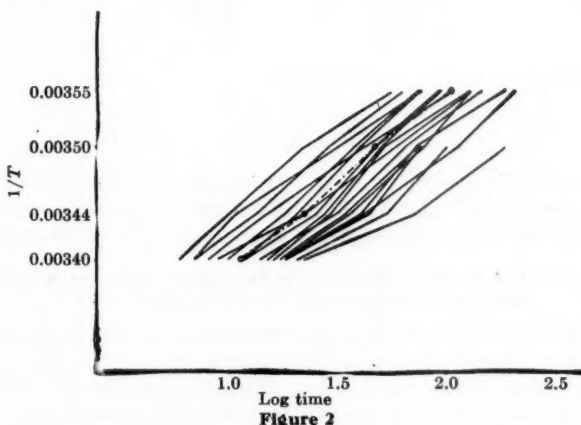
$$\frac{d \log t}{d \left(\frac{1}{T} \right)} = 6.53 \times 10^3$$

Since $\log e$ is known (0.43429) and R is a molecular constant, it must be possible to calculate the energy of activation of the contacts of flocculated rubber particles resulting in agglutination.

The most important point in this connection is, however, that it is possible to express the effect of temperature on the time of coalescence by the formula of molecular reactions, and that the equation

$$t = A_2 e^{\frac{E}{RT}}$$

applies likewise to the coalescence phenomenon.



In this case

- t = the time required for coalescence, measured at the instant of agglutination of the flocculated particles
- T = the temperature (absolute)
- A_2 = a constant which depends on the concentration of the latex and on the acidity
- $\frac{E}{R}$ = the energy-impact constant

The constant A_2 is positive, and increases in magnitude with increase in concentration of the latex and with reduction in acidity.

de Vries and Beumée-Nieuwland⁹ have already studied the influence of temperature on coalescence by inoculation with "B" liquid. Although in their experiments the time required for coalescence to take place was not based on a constant acidity, and although the various measurements show in some cases unexplainable variations and inconsistencies, it is still of importance to examine their experimental results more closely.

In the following table a few of their series of experiments are summarized.

Temperature	25	30	35	40	45	50	55	60	65	70	75	80	85	90
Time of coalescence (min.)	105	67	55	42	37	32	21	25
Time of coalescence (min.)	91	41	17	12	7	4	2
Time of coalescence (min.)	...	50	32	21	16	?
Time of coalescence (min.)	62	39	30	20	17

In Fig. 3 the logarithms of time are shown as a function of the reciprocals of the absolute temperatures ($1/T$).

Temperature (Celsius)	Reciprocal Values (Absolute Degrees)	Temperature (Celsius)	Reciprocal Values (Absolute Degrees)
25	0.00336	60	0.00300
30	0.00330	65	0.00296
35	0.00325	70	0.002915
40	0.003195	75	0.00287
45	0.003145	80	0.00283
50	0.00310	85	0.00279
55	0.00305	90	0.00275

In spite of slight anomalies, the formula

$$t = A_2 e^{\frac{E}{RT}}$$

represents satisfactorily, over the wide temperature range of 25° to 90° C., the experimental data of de Vries and Beumée-Nieuwland, since calculation of $\log t$ and $1/T$ showed that they are linear functions of one another (see Fig. 3).

Hydration of the Rubber Particles in the Latex of *Hevea Brasiliensis*, and the Separation of the Hydratant Acid

In Chapter IV of "The Electrometric Determination of the Hydrogen Ion Concentration in the Latex of *Hevea brasiliensis* and Its Applicability to Technical Problems,"¹ the observations of de Vries, Belgrave, and Beumée-Nieuwland are discussed fully in their relation to the existence of hydratants in latex.

Memmler¹⁰ and Marchionna¹¹ give several references to the literature, not all of which are available to the present author, wherein the isolation from latex of various non-rubber components, including resins, proteins, sugars, organic acids, dyes, enzymes, and inorganic substances, is described. Of particular importance in connection with hydratants are the publications of Bishop and Belgrave,¹² Belgrave,¹³ and Bruni and Levi.¹⁴ Recent data on latex are to be found in publications by Génin,¹⁵ Dawson and Porritt,¹⁶ Noble,¹⁷ and Stevens and Stevens,¹⁸ while studies by Rhodes and Wiltshire¹⁹ and by Rhodes and Bishop²⁰ on the lipin complex are worthy of attention. Roberts in a series of articles²¹ discusses the composition of latex.

In view of earlier investigations by Eaton, Grantham, and Day,²² Vernet,²³ Bishop,²⁴ and de Vries and Beumée-Nieuwland²⁵ on the determination of rubber in latex by freezing it out of the latex, experiments were carried out by the present author with the object of separating rubber as a coagulum at low temperatures and thus separating the serum in a more or less clear state for studying the hydratants.

Field latex with a hydrogen-ion concentration of $p_H = 7.03$ at 27° C. was chosen as a starting point. The latex was kept in the freezing chamber of a refrigerator

for fourteen days at -5°C ., and then was cautiously thawed at 5°C . By this treatment the rubber agglomerated to a compact lump; the light yellow, nearly transparent serum had a hydrogen-ion concentration of $p_{\text{H}} = 6.98$ at 27°C ., and it contained considerable protein which could be precipitated by alcohol, and which accounts for the characteristic odor of fresh latex.

The p_{H} value of the serum was closer to that of the original latex than are the values of Bishop ($p_{\text{H}} = 6.5$) and de Vries ($p_{\text{H}} = 6.2$), and it agrees better with the slightly alkaline reaction of fresh latex.

Since the method of concentration of the serum for the purpose of isolating the hydratant was extremely complicated, and was applicable only to small quantities of serum, experience already acquired²⁶ in work on centrifuged latex, creamed latex, and underlatex was utilized as a starting point for the separation of the hydratant.

Latex with a dry rubber content of 34.26 per cent was centrifuged without the addition of any anticoagulant or antiseptic. This centrifuging gave a cream with a

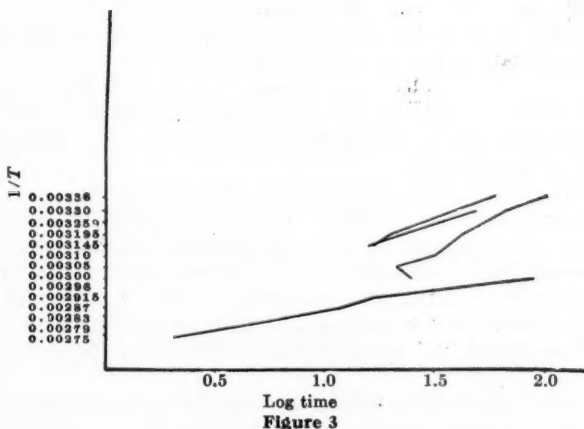


Figure 3

dry rubber content of 55.35 per cent and an underlatex containing 5.37 per cent of rubber. The mucilaginous sludge which was deposited in the centrifuge was also collected.

Latex, cream, underlatex, and sludge were kept for 24 hours at 0°C .

The sludge soon turned dark blue without coagulating; it was brittle and contained no rubber. However, it did contain a considerable quantity of peroxidases,²⁷ which have been studied in detail by Bobilioff.²⁸

After a few hours the underlatex coagulated with a blue tint, the field latex coagulated after 18 hours at 0°C . with a light blue tint, while the cream remained in an uncoagulated state and became only slightly discolored.

The percentages of enzymes and of decomposable proteins diminished in the following order:

Sludge > underlatex > field latex > cream

After the serum of the spontaneously coagulated field latex, the serum of the underlatex, the uncoagulated cream, and the sludge had been held at 0°C . for 18 hours, coalescence tests were made with similar quantities of "B" liquid having a hydrogen-ion concentration of $p_{\text{H}} = 4.37$. In this case the quantities of field

latex serum, of underlatex serum, and of cream which were added were calculated from the original dry rubber content in the base product.

Quantity of Inoculating Liquid, Calculated on the Dry Rubber Content	Minutes Required for Coalescence of "B" Liquid at 27° C.		Rubber Cream
	Field Latex Serum	Underlatex Serum	
1	...	300	...
2	...	90	...
3	...	40	...
4	...	25	...
5	300	20	...
6	260	17	...
7	230	15	...
8	200	13	...
9	180	11	...
10	160	10	300
20	80	5	100

The data in the table above show that the coalescing powers of the three liquids tested, viz., field latex serum, underlatex serum, and cream, stand, when calculated on a dry rubber basis, in the ratio: 80:5:100 or 16:1:20.

The serum of the spontaneously coagulated underlatex contains therefore sixteen times as much hydratant as does the serum of field latex.

Coalescence tests of the sludge from the centrifuge, both in its normal state and after extraction with N NH_4OH or $2 N$ NaOH , gave no positive results. The concentration of hydratant in the brittle sludge is evidently so low that the effect on the "B" liquid is inappreciable.

Attempts were then made to obtain larger quantities of the serum from the spontaneous coagulation of underlatex. To this end, underlatex was kept in a refrigerator at 2° C., as a result of which it coagulated spontaneously within two hours. The serum of this coagulum, which had a fresh odor and a p_H value of 6.90, was expressed from the coagulum, and was treated with $2 N$ HCl until no further precipitation occurred. It was then washed thoroughly with dilute hydrochloric acid on a Büchner funnel, and extracted with warm alcohol for several hours in a Berntrop flask.

From the alcohol there was obtained 35 milligrams of a substance which was difficultly soluble in alcohol but was easily soluble in alkalies. After evaporation the solution neutralized by potassium hydroxide yielded a residue which was more or less resinified. None of the products had any coalescing effect on "B" liquid after precipitation with hydrochloric acid, so that extraction with alcohol was unnecessary.

When the precipitate obtained by hydrochloric acid was dissolved directly in an alkali, the resulting solution had a weak coalescing action.

In experiments with serum obtained by freezing underlatex without evaporation, there was obtained, after thawing, a product which possessed only a slight coalescing power. On the other hand when the cake of rubber obtained from underlatex was extracted with potassium carbonate solution, a frothy extract with strong coalescing power was obtained. When this extract was precipitated by hydrochloric acid and the precipitate was dissolved in a minimum of potassium hydroxide solution, the product was found to have, at an acidity of $p_H = 4.37$, a very rapid, and, at an acidity of $p_H = 4.57$, a somewhat slower coalescing action on "B" liquid.

The Natural Hydratant Present in Concentrated Form in the Coagulum of Underlatex

The isolation of hydratant was carried out in the following way. Field latex was centrifuged slowly without the addition of any chemical reagent whatsoever,

i. e., at a slow rate of addition at the normal r. p. m. (see the description of this process in the treatise on "The Electrometric Determination of the Hydrogen Ion Concentration in the Latex of *Hevea brasiliensis* and Its Applicability to Technical Problems," p. 319¹).

The underlatex was collected and kept for two days at 10° C. in a refrigerator. The rubber which coagulated spontaneously from this underlatex was sheeted out very thin, and was washed thoroughly with water. The washed yellow crepe was cut into pieces and extracted for 24 hours at 10° C. with 10% potassium carbonate solution.

The extract was acidified cautiously with 10% hydrochloric acid to the point at which evolution of gas ceased, and was then agitated vigorously, whereupon a flocculent precipitate formed. After decantation this precipitate could be readily filtered on a folded filter, after which it was washed thoroughly on the filter with distilled water until neutral. The filtrate was clear, while the precipitate was a dry light yellow, amorphous, non-mucilaginous mass.

When dissolved in potassium hydroxide solution, the precipitate had a very strong coalescent effect on "B" liquid of various degrees of acidity. As a low acidity of $p_H = 4.57$, 0.5 cc. of a 10% solution of the precipitate coalesced 50 cc. of "B" liquid within 30 seconds, whereas untreated "B" liquid showed no tendency to cohere even after 24 hours.

Two cc. of the serum of this coalesced product coalesced 50 cc. of "B" liquid with a p_H value of 4.57 within 12 hours, indicating that there was a large excess of hydratant present. The resulting mass was removed from the filter, was spread out on a glass plate, and was dried at 25° C. in a vacuum. The product was a light brown powder, the odor of which resembled that of ordinary crepe rubber dried in a rubber drying house.

The yields of the product, compared with those from field latex, are shown in the following table:

Field Latex (Kg.)	Underlatex (Kg.)	Crepe Rubber from the Underlatex Dried Coagulum (Kg.)	Yield of Dry Hydratant (Grams)
40	12.0	1.050	4.21
40	11.2	0.750	3.62
40	11.6	0.770	3.28
40	11.7	0.725	3.20
40	10.9	0.680	2.94
40	11.2	0.675	3.04
40	13.5	1.520	2.08
40	12.1	1.310	3.36
40	10.8	0.760	1.88
40	11.9	1.150	4.79
80	24.0	1.950	5.33
80	23.5	1.860	5.12
80	23.6	1.900	4.87
80	21.9	1.730	4.53
80	23.1	1.775	5.06
80	20.8	1.740	5.27
80	22.3	1.835	5.98
960	276.1	22.180	68.54

Accordingly 68.54 grams of hydratant were isolated from 960 kilograms of field latex, i. e., approximately 0.007% of the latex and 0.31% of the dry rubber in the coagulum from the underlatex.

Attempts were then made to purify the product by further precipitations. However, the substance showed itself to be completely insoluble in various solvents,

both when cold and warm; *e. g.*, water, ether, alcohol, benzine, benzene, chloroform, and acetic acid did not dissolve it.

On the other hand it dissolved immediately in aqueous alkalies and in alkaline carbonates. In this case it was necessary to acidify the solutions very strongly to reprecipitate the substance. This altered its character, and it was difficult to filter. Difficulties were also encountered in determining its melting point. At 150° C. it formed decomposition products, of a character which indicated the presence of complexes containing nitrogen. At 255° C. the substance fused completely, and at higher temperatures it decomposed, with formation of a liquid and a hard coal-like cake.

The aromatic test of Guerbet²⁹ was negative, so that tyrosine, tryptophan, and phenylalanine could not have been present. Filtration with potassium hydroxide solution according to the formaldehyde test for amino acids³⁰ gave good indications that an amino acid was present.

After drying the powder at 250° C. over calcium chloride in a desiccator, the product was dried at 100° C. to constant weight in a drying oven. A further loss of 2 to 4 per cent by weight took place.

Elementary analysis of the product led to difficulties because of its resistance to attack by reagents, its decomposition, and its carbonization. By combustion in a current of oxygen and use of the ter Meulen and Heslinga method,³¹ and by the Kjeldahl method as modified by Wilfarth-Kulisch,³² the following average results of a series of analyses were obtained:

Carbon	57.18%
Hydrogen	10.17
Oxygen	25.21
Nitrogen	7.44
	<hr/> 100.00%

It is absolutely necessary to store the underlatex coagulum in the cold, to prepare the extract as rapidly as possible, and to dry the precipitate immediately. The product is an excellent nutrient medium for molds and other microorganisms, and it was found that a product dried slowly contained a lower percentage of nitrogen and harbored mold growths. Thus during two days' storage in dampness, the nitrogen decreased to 5.93 per cent, and after 1 week to 4.81 per cent.

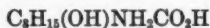
When the hydratant was allowed to stand in potassium carbonate solution for a few days at 25° C., ammonia was evolved, and when hydrochloric acid was added to this decomposed solution, a white turbidity ultimately appeared, but no precipitate as with freshly prepared substance. With a large quantity of hydrochloric acid, a precipitate appeared after one week; this precipitate contained only 2.54 per cent of nitrogen, and was difficult to filter.

The hydratant may have a molecular composition as follows:

$$\text{C} \frac{57.18 \times 14}{12 \times 7.44} \quad \text{H} \frac{10.17 \times 14}{7.44} \quad \text{N } 1 \quad \text{O} \frac{25.21 \times 14}{16 \times 7.44}$$



Considering that the substance has the character of an amino acid, its constitution in simple form may be:



i. e., an *aminohydroxypelargonic acid*.

The term *hydratant acid* or *H acid* is proposed for this acid. A more exact deter-

mination of the structure was impossible with the apparatus and the small quantity of product available, but in a later publication the subject will be discussed further.

The origin and the structure of this hydratant acid in latex can be explained on the basis that it is a decomposition product of proteins in the latex serum, the A, B, and C types of which contain, according to Bishop, 14.0–15.1, 15.4–14.5, and 16.9–16.4 per cent, respectively, of nitrogen. Important data have been published by Pohlmann,³³ Plimmer,³⁴ Pauli and Valke,³⁵ and Gerngross³⁶ on the formation of amino acids from proteins and on their classification. In this type of decomposition, enzymatic processes may play a part. It is improbable that tyrosinase, to which de Jong³⁷ calls attention, can be the direct cause of a cleavage of protein to an aminohydroxypelargonic acid having a coalescing action, since the acid which was isolated contained no aromatic nucleus.

de Jong found that, when trees were tapped with several superimposed cuts, the latex from the uppermost cut was colored, whereas the latex from the lowest cut was not tinted. This discoloration depends on a lack of tyrosine in the latex. The white latex could not be coagulated by acetic acid.

In continuing the tapping experiments of de Jong, van Dillen³⁸ found that, with small trees, the latex from a cut between two rings would not coagulate but would only flocculate; in other words, there was no coagulating agent present, and correspondingly there was no discoloration.

When no enzyme with power to bring about cleavage of proteins is present, no hydratant acid is formed, and there is no coalescence.

It is noteworthy that the proteins do not play a primary role in the coagulation of the latex of *Hevea brasiliensis*, but rather a secondary part by the formation of hydratant acid and by the fact that in the absence of this acid, as in the cream obtained by centrifuging field latex, good coalescence of the rubber particles is prevented. The results of the present investigation throw new light on the theory of coalescence of de Vries.³⁹ There is no direct mechanical relation between enzymes and coalescence, although by the action of enzymes (coalase) the still undefined proteins are decomposed into hydratant acid, which in turn brings about coalescence.

Accordingly enzymes have primarily a secondary function, and from this point of view the coalase theory is necessarily subject to modification.

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- ²⁷ With regard to peroxidases in the sludge from dairy centrifuges, see Hijlkema, "Leerboek der Zuivelbereiding," **1923**, p. 177.
- ²⁸ Bobilioff, *Arch. Rubbercultuur*, **8**, 817 (1924).
- ²⁹ Schoorl, "Organische Analyse," **I**, 66 (1935).
- ³⁰ Meyer-Jacobson, "Lehrbuch der organischen Chemie," **I**, 735 (1923).
- ³¹ ter Meulen and Heslinga, "Nieuwe Methoden voor Elementairanalyse," 2nd Ed., **1930**, p. 11.
- ³² Berl-Lunge, "Chemisch-Technische Untersuchungsmethoden," **III**, 1932, p. 601.
- ³³ Pohlmann, "De Scheikunde der Eiwitten," **1924**.
- ³⁴ Plimmer, "The Chemical Constitution of Proteins," **1913**.
- ³⁵ Pauli and Valke, "Kolloidchemie der Eiweisskörper," **1933**.
- ³⁶ Ullmann, "Enzyklopadie der technischen Chemie," **IV**, 334.
- ³⁷ de Jong, *Mededeelingen van het Agricultuur-Chemisch Lab.*, **10**, 48 (1915).
- ³⁸ van Dillen, "Handelingen van het Derde N. I. Naturwetenschappelyk Congress," **1924**, p. 268.
- ³⁹ de Vries, *Arch. Rubbercultuur*, **8**, 219 (1924).

The Concentration of Latex by Creaming

H. C. Baker

Latex consists of a suspension of microscopic particles of rubber, bearing an adsorbed layer of protein, in an aqueous serum containing principally *l*-methyl inositol, so-called rubber resins, and saline substances. The rubber particles are in continuous oscillatory motion, which may be seen under the microscope. Brownian movement is due to the bombardment of the suspended particles by the molecules of the dispersion medium, and it can be demonstrated that the smaller particles are in more violent oscillatory movement than the larger particles. The rubber particles in latex are sufficiently small to remain in suspension in the aqueous serum for an indefinite period, but if latex is left to stand, a concentration gradient will develop throughout its bulk, leading to the formation of an upper concentrated layer of closely packed rubber globules in a manner analogous to the formation of cream on milk. This behavior is shown by all types of latex, field, preserved, and concentrated, but the effect is stated to be much greater with preserved latex than with field latex (Bishop and Fullerton, *Latex Preservation and Shipment Planting Manual*, No. 4, Rubber Research Institute of Malaya, July, 1932). The same authors give figures (Table I) which show the magnitude of this effect for freshly ammoniated latices which had remained undisturbed for a period of two months. It will be observed that creaming occurred to a considerable extent in all samples, accompanied by a diminution in the ammonia contents of the surface layers.

The natural gravitational tendency of rubber globules to rise to the surface of the serum may be artificially increased by centrifuging, whereby the latex is separated into a cream containing 60 per cent or more of rubber, and a skim containing 10 per cent or less of rubber, together with most of the non-rubber serum components. The modified milk centrifugal separator devised by Utermark for this purpose (English Patent 219,635 (1923)) started the extensive research which has led to the commercial development of the centrifugal method of creaming latex.

TABLE I
NATURAL CREAMING OF LATEX (Bishop and Fullerton)

Sample No.	Freshly Prepared		After 2 Months' Storage		Lower Layer Dry Rubber Content %
	Dry Rubber Content %	Ammonia (NH ₃) %	Surface Layer Dry Rubber Content %	Ammonia (NH ₃) %	
1	39.17	0.43	75.20	0.20	15.26
2	39.49	0.52	74.30	0.23	17.13
3	39.93	0.41	75.21	0.20	12.02
4	38.89	0.45	73.50	0.19	21.34
5	38.61	0.44	73.27	0.19	16.15
6	38.46	0.47	75.93	0.20	13.46
7	38.78	0.43	75.97	0.21	14.38

The analogy between rubber latex and milk led Traube (English Patent 226,440 (1924)) to investigate the action on latex of vegetable mucilages, which had recently been shown to accelerate the formation of cream on milk. Their effect was to cause latex to separate into two well-defined layers, an upper layer containing nearly all

the rubber in a concentration of from 55 to 60 per cent above a lower translucent almost rubber-free layer. Traube's patent covered vegetable mucilages in general, and particularly, Carragheen and Iceland mosses, and also gelatin and glue. The method of application was to mix latex with about one-seventh of its bulk of a one per cent solution of Carragheen moss and heat the mixture for some hours at 40° to 60° C., when the separation into two layers occurred. Although none of the substances mentioned by Traube had much practical application, his invention gave the impetus to the search for new and better creaming agents, owing to the ease with which creaming could be carried out on estates, without requiring expensive apparatus.

Natural Creaming Agents.—Substances which have been described in patent literature as creaming agents, in addition to those mentioned by Traube, are gum arabic, pectin, gum tragacanth, gum Karaya, alginic acid and alginates, and lately tragon seed gum.

Considerable difficulty was experienced by estates in the early days of the development of the creaming process, owing to variability of the creaming agent. This is well illustrated by the results of the examination at the Imperial Institute of 25 samples of gum tragacanth obtained from different sources, the examination being made by the method recommended by Bishop and Fullerton (*loc. cit.*). Four of the samples gave a cream below 50 per cent, eleven between 50 and 60 per cent, and the remaining ten gave over 60 per cent of dry rubber in the cream. Roughly one-third were definitely unsatisfactory, giving creams containing less than 55 per cent of dry rubber.

Similar variations were observed between different grades of gum Karaya, and no creaming action was obtained with samples of gum arabic and agar-agar, both of which have figured in patent literature as creaming agents. No information is available, however, regarding the variation which may occur with pectin and the alginic acid series of creaming agents. Alginic acid is extracted from certain species of seaweeds, and ammonium alginate has been used on American-owned plantations in Sumatra (English Patent 294,002 (1927)); so far as is known it is not used in Malaya.

The lack of reliability shown by many of the vegetable gums as creaming agents led to a search at the Imperial Institute for new and dependable products (English Patent 450,222 (1935)).

Natural creaming agents such as gum tragacanth are highly complex substances of the carbohydrate type, which may contain acidic or alkyl groupings. It seemed, therefore, possible that plant lignins, which may contain 40 carbon atoms and several methoxyl groups, might function as creaming agents. These are extractable from plant tissue with dilute caustic soda, and it was found that the caustic soda extract of oat straw creams preserved latex. When lignin was prepared from oat straw, however, by the sulfuric acid method, no creaming action could be obtained. Oat straw was, therefore, freed from pectin and lignin by extraction first with ammonium oxalate solution and then with alcoholic caustic soda. A slight creaming action was shown by these fractions, but by far the greatest action was obtained with the caustic soda extract of purified oat straw, which contained the hemicelluloses present in the straw. These are substances which, from a study of the literature, appear to be essentially similar chemically to natural creaming agents such as those present in vegetable gums and mosses.

Materials containing hemicelluloses, such as oat, wheat, and barley straws; castor, rape, cotton, soya bean cake meals; copra, wheat chaff, bean pods, hops, brewers' grains; beech and birch sawdust; old rubber seed, shells, and kernels were treated (a) with 0.5 per cent ammonium oxalate solution to remove pectins, (b)

with 50 per cent aqueous alcohol containing 1 per cent caustic soda to remove the more soluble lignins, (c) with 4 per cent caustic soda solution to extract the hemicelluloses. Two or three extractions of each type were made at 80° C. The final caustic soda solution was neutralized with glacial acetic acid, and any precipitate collected (hemicellulose A); half its bulk of acetone was added to the filtrate when hemicellulose B was precipitated; a further half volume of acetone was added to the final filtrate in order to precipitate hemicellulose C.

Negative results were obtained with castor and rape seed meals, wheat chaff, hops, birch sawdust, old rubber seed, shells, and kernels. The other materials treated gave creaming agents in varying yields, and the most promising was that obtained in about 10 per cent yield from brewers' grains.

Linseed cake meals were also examined, and creaming agents prepared from eight meals obtained from different sources. One set was prepared by the evaporation of cold-water extracts of the meals and a second set by purification of aqueous extracts by precipitation into alcohol followed by filtering, washing with alcohol and ether, and drying. The yield of crude extract was from 13.7 to 21.9 per cent by weight when 125 grams of meal were treated with 4 liters of cold water, with intermittent stirring for 24 hours. The yield of purified materials varied from 53 to 82 per cent of the crude extract, and the average figure of 70 per cent was exceeded in five cases out of the eight. When the creaming agents were tested on preserved latex, no difference in creaming action was observed between crude and purified materials, but when tested in the East on field latex the purified materials showed a definitely improved performance over the crude extracts (Table II). Further experiments on the extraction of linseed meals with dilute ammonia showed that a better creaming agent might be obtained than by aqueous extraction.

TABLE II
THE CREAMING OF LATEX WITH LINSEED MEAL EXTRACTS¹

Sample	Parts Creaming Agent per 100 Parts Latex	Best Dry Rubber Content of Cream	Dry Rubber Contents of Control ²
<i>Crude Extracts</i>			
A	0.3	58.5	58.8
B	0.3	58.4	58.8
C	0.3	55.1	57.8
D	0.3	51.4	57.3
E	0.3	55.1	57.3
F	0.3	56.6	57.5
G	0.3	57.9	58.5
H	0.3	58.5	58.5
<i>Purified Extracts</i>			
A	0.2	58.5	58.8
B	0.2	58.7	58.8
C	0.3	58.2	57.3
D	0.3	57.9	57.3
E	0.3	58.7	57.5
F	0.3	59.3	57.5
G	0.2	59.9	58.5
H	0.2	59.8	58.5

¹ Experiments carried out by Edgar Rhodes of the Rubber Research Institute of Malaya.

² Control was tragon seed gum at a concentration 0.3 part per 100 parts of latex-water phase, i. e., approximately 2 parts per 100 parts of latex.

Attempts have been made to prepare creaming agents by chemical modification of naturally occurring substances in order to obtain the characteristics of vegetable gums. The latter form viscous colloidal solutions with water and are usually

of complex carbohydrate character, sometimes in association with one or more metals, such as potassium and magnesium. Cellulose is a high molecular weight carbohydrate, but is itself insoluble in water. On introducing methyl groups into the molecule, however, the methyl cellulose is capable of forming a viscous colloidal solution with water, and of creaming latex. Methyl cellulose is not however as efficient as the natural gums, and creams obtained with its aid rarely exceed a dry rubber content of 55 per cent in the normal creaming period; further, the concentrate is very liable to "after-creaming." One batch examined at the Imperial Institute creamed on standing for three months from 55 to 62 per cent, above a clear dark brown serum. In contrast to the methyl derivatives, ethyl cellulose, although water-soluble, has not been found to cream preserved latex; it is difficult, however, to suggest a reason for this.

Starch is also a high molecular carbohydrate, differing from cellulose in the smaller size of its molecule, and having an α -glucose unit instead of a β -glucose unit. As the molecules of cellulose and starch are composed of a large number of glucose units, it is possible to introduce into the molecule any fraction of the maximum number of methyl groups which are theoretically possible, and so obtain compounds varying in methoxyl content from 0 to 45.6. The preparation of methyl and ethyl starches and their use as creaming agents were studied by the writer in the laboratories of Professor Haworth at Birmingham University. Creaming with preserved latex was observed with compounds ranging from 6 to 34 per cent methoxyl content; the efficiency was approximately the same up to about 24 per cent methoxyl content, but thereafter decreased. When the methylated starches were tested on fresh field latex, their efficiency was found to be considerably reduced, and maximum activity appeared to be at about 20 per cent of methoxyl. It was concluded from this investigation that methyl or ethyl starches are of similar creaming power to methyl cellulose and would not be able to compete with the best vegetable gums for efficiency, although it would probably be possible to produce a standard material. The recent discovery of tragon seed gum by the Rubber Research Institute of Malaya, however, has altered the position regarding the need for reliable alternatives to the vegetable gums (English Patent 430,935 (1934)). Tragon seed gum regularly gives creams of 58 per cent dry rubber content, and is a well-known creaming agent in Malaya. Several samples have been examined at the Imperial Institute and all have been found satisfactory.

Recently the United States Rubber Company has also added to the list of vegetable extracts by introducing those prepared from the seeds of plants of several botanical species: of the order Leguminosæ, the genus *Cassia* (English Patent 448,244 (1934)) and the tribe *Eucæsalpinix* (English Patent 448,203 (1934)); and of the order Arales, the tribe *Amorphophallus* (English Patent 448,245 (1934)). Seeds from the genus *Poinciana* Regis belonging to the tribe *Eucæsalpinix* are described as giving creams containing 66 per cent dry rubber after 6 days.

Synthetic Creaming Agents.—Synthetic creaming agents are described in English Patent 429,559 (1934) of the Metallgesellschaft A-G., which claims all synthetic water-soluble colloids whose molecules are "polymer-homologous," i. e., those which are composed of a number of chemically identical units, and differ only in their degree of polymerization. Specific compounds mentioned are the polyacrylic acids and their salts, polyvinyl alcohols and their ethers, and polyethylene oxides and their derivatives. From the examples given in the patent, these materials appear to be similar in efficiency to methyl starch or cellulose in their creaming action on latex.

Improvements in the Creaming Process.—When a creaming agent is added to fresh field latex, separation into cream and serum does not occur at once, but an

induction period of some hours elapses before creaming becomes evident. The length of the induction period diminishes with the age of the latex, and in this country ammoniated latex usually shows appreciable creaming in from one to two hours after the addition of the creaming agent. Improvements in the creaming process have been directed towards reducing the induction period, and increasing the dry rubber content and stability of the cream. Many of the patented processes have been claimed to effect one or more of these improvements.

It has been proposed to decrease the induction period experienced with field latex by subjecting the latex, either before or after the addition of creaming agent, to violent agitation by stirring for about 30 seconds at speeds of several thousand revolutions per minute. Not only is the induction period shortened but it is claimed that the whole process is accelerated, and that a cream with a higher dry rubber content is produced (English Patent 417,162 (1933)). In English Patent 344,647 (1930), the Naugatuck Chemical Co. proposes to submit the mixture of latex and creaming agent to a low potential difference between two large-surface electrodes, in such a manner that little electrical energy is consumed. It is claimed that the time then required to concentrate the latex is from 5 to 25 per cent of the normal for the particular creaming agent used. Thus, a cream of 55 per cent of rubber may be obtained in from one to two hours instead of twenty-four.

English Patent 413,185 (1933) deals with the use of soaps, such as ammonium oleate, and volatile alcohols, such as cyclohexanol, in conjunction with the creaming agent. By this means it is claimed that the induction period is eliminated, and the resulting cream is rendered stable by the cyclohexanol. On drying, the ammonia and cyclohexanol evaporate, but the oleic acid remains in the films.

Another process describes the use of weak acids, such as citric, malic, etc., as a small percentage of the creaming agent, in order to facilitate the creaming process. It has also been suggested to use the serum from one creaming operation to cream a fresh lot of latex (United States Rubber Co., U. S. Patent 1,777,045 (1930); 1,772,752 (1930)).

Experiments have been made at the Imperial Institute to increase the dry rubber content of the cream by a modification in technic. Reference has been made to a concentration gradient existing in undisturbed creamed latex; the magnitude of this is shown in Table III. In fully creamed latex it will be seen that the range

TABLE III
CONCENTRATION GRADIENT IN GUM TRAGACANTH CREAM

Location of Sample in Cream	Dry Rubber Content after Standing for Periods of			
	18 Hours	42 Hours	66 Hours	12 Days
Top	57.80	59.61	60.58	62.36
1st Quarter	56.08	59.28	60.12	62.09
2nd Quarter	55.24	58.65	59.64	61.90
3rd Quarter	55.05	58.62	59.69	61.80
Bottom	54.71	57.89	59.38	...

of dry rubber content is quite small, the high concentration of the cream being maintained to within a fraction of an inch of the lower level of the cream. It was sought to remove the top layer of cream, of maximum dry rubber content, while introducing fresh latex mixed with creaming agent just above the division of cream from serum, at the same time removing serum at an appropriate rate. It was difficult to control the rates of flow necessary in a small apparatus, which could, moreover, only be run for a working day at a time, but results were, nevertheless, obtained which indicated that with a larger apparatus it would be possible to with-

draw the upper layer of cream at a rate which would maintain its initial high dry rubber content.

The improvements so far discussed are applicable to creaming generally, but methods are also available for improving the rate of creaming and final concentration when latex is treated with a particular creaming agent. An example of such a process is the use of ammonia to the extent of 1.5 per cent with tragon seed gum, in place of the 0.7 per cent normally used. In addition the stability of the cream is improved, and none of the consignments creamed by this method which have been examined has shown any signs of "after-creaming." A similar process involves the use of acetone or ethyl alcohol in amounts up to 5 per cent of the latex in conjunction with gum tragacanth as creaming agent. The addition of acetone or alcohol was shown to have no detrimental effect on the stability of the cream. (Rubber Research Institute of Malaya, English Patent 430,935 (1934); 415,133 (1933).)

Practical Aspects of Creamed Latex.—Creamed latex may be used for all operations which require concentrated latex, and in addition for special processes where a very pure rubber is required. Concentration of latex by creaming and centrifuging results in the removal of some of non-rubber substances which are retained in the skim fraction. The progressive purification of latex by repeated creaming is shown in Table IV (McGavack, *Ind. and Eng. Chem.*, 27, 894 (1935)),

TABLE IV
THE PROGRESSIVE PURIFICATION OF LATEX BY CREAMING (McGavack)

Latex	Acetone Extract %	Nitrogen %	Ash %	Water Absorption after 100 Hrs. at Room Temperature
				Mg. per Sq. Cm.
Normal	5.20	0.70	1.0	13.5
Once-creamed	3.54	0.33	0.42	8.9
Twice-creamed	2.83	0.24	0.15	3.6
Thrice-creamed	2.48	0.10	0.09	1.8

and a comparison of the nitrogen contents of creamed and centrifuged latices in Table V (Boggs and Blake, *Ind. and Eng. Chem.*, 28, 1198 (1936)). After nine centrifugings Kemp (*Rubber Age* (N. Y.), 40, 366 (1937)) obtained a cream, the rubber from which was ash-free and contained 0.056 per cent nitrogen. In contrast to the multi-centrifuging of latex, it is possible to cream latex for a limited number of times only, usually three or four, as above this number the creaming agent no longer causes separation into two layers. The purification of latex by triple-creaming has been developed commercially for the manufacture of wire insulation by a dipping process and the preparation of rubber for other purposes requiring a low water-absorption.

TABLE V
PURIFICATION OF LATEX BY CREAMING AND CENTRIFUGING (Boggs and Blake)

Times Treated	Nitrogen Content	
	Creamed	Centrifuged
0	0.70	...
1	0.33	0.20
2	0.24	0.14
3	0.10	0.098
4	..	0.088
5	..	0.080

As regards the economics of the creaming process, only a small proportion of creaming agent is required per pound of rubber and perhaps extra ammonia. Ini-

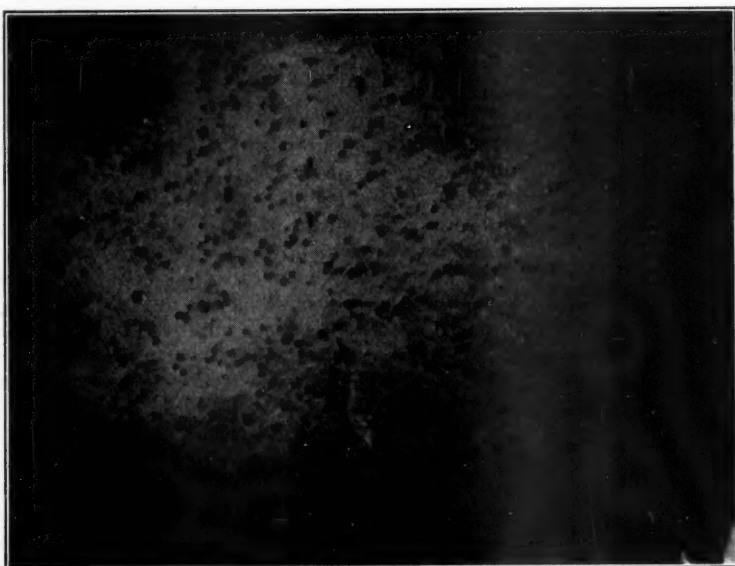


Figure 1
(Magnification, 740 diameters)

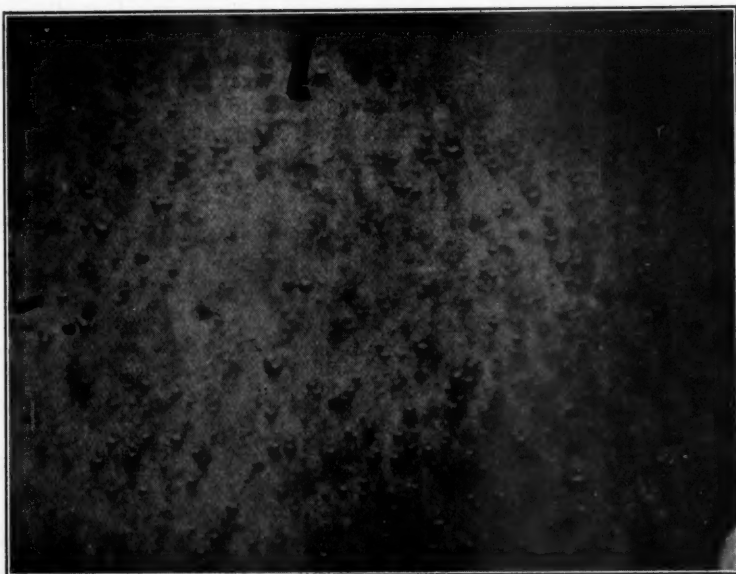


Figure 2
(Magnification, 740 diameters)

tial costs are low, so that economically creaming compares very favorably with other concentration processes. The subject is dealt with more fully by Bishop and Fullerton (*loc. cit.*).

Creaming as an Aid to Research.—During his work on the preservation of latex with caustic soda, de Vries (*Arch. Rubbercultuur*, 9, 714, 750 (1925)) discovered its ability to act as a creaming agent when present in sufficient concentration. Pummerer and Pahl (*Ber.*, 60, 2152 (1927)) made use of the creaming action of caustic soda on latex, and the simultaneous removal of protein which accompanies it, to obtain a purified latex to study the sol and gel phases of the rubber hydrocarbon. Latex containing caustic soda in 2 per cent concentration was heated for several hours at 60° C. in an atmosphere of nitrogen and then allowed to cream at room temperature. After several treatments of this nature, followed by dialysis to remove the caustic soda, the latex gave a rubber which was nitrogen free and had an ash content of 0.1 per cent. This process has been improved by Smith, Saylor, and Wing (*Bur. of Standards, J. Research*, 10, 479 (1933)), who found that a purified latex could be obtained by the action of the enzyme trypsin at a temperature of 38° C. The latex was washed free of the hydrolyzed protein by creaming with caustic soda several times as in Pummerer's process, and then dialyzing.

The Mechanism of Creaming.—Creaming has been shown to be caused by caustic soda, and other non-colloidal substances quoted in this connection are potassium carbonate (Stevens, *Bull. Rubber Growers' Assoc.*, 5, 216, 450 (1923)) and buffer solution mixtures, *e. g.*, of primary and secondary sodium phosphates (Smith, U. S. Patent 1,678,022 (1928)). Caustic soda creams are liable to flocculation, and never exceed a concentration much in excess of 60 per cent even when in the form of a stiff paste (de Vries, *loc. cit.*). The theoretical figure for the close-packing of spherical globules has been calculated by Ostwald (*Kolloid-Z.*, 6, 105 (1910)) to be 78 per cent by volume, and a dry rubber content of 60 per cent in a caustic soda cream would amount to 65 per cent by volume, when allowance is made for the higher specific gravity of the serum. These facts suggest that this type of creaming is an enhanced natural creaming due to an aggregation of the particles caused by chemical action on the surface layer, coupled with considerable hydration of the particles. The increase in density of the serum, which may be appreciable, also facilitates the creaming.

TABLE VI
CARBOHYDRATES AND THEIR DERIVATIVES WHICH CREAMED PRESERVED LATEX

Substances	Concentrations Referred to Gum Trag. = 1	Creaming Action
Methylated xylan	5 and 25	5 negative; 25 fair
Arabic acid	5 and 25	5 weak; 25 strong
Degraded arabic acid	5 and 25	5 negative; 25 fair
Methylated arabic acid	5 and 25	5 negative; 25 weak
Aldobionic acid from gum arabic	40	Fair
Yeast mannan	25	Strong
Lichenin	2 and 4	2 weak; 4 fair
Ash-free lichenin	2 and 4	2 very weak; 4 weak
Luteic acid	2 and 4	2 weak; 4 fair

Creaming by high-molecular weight colloids might be thought to be connected with their chemical constitution, as all the known natural creaming agents are complex carbohydrates. Through the courtesy of Professor Haworth of Birmingham University it was possible to examine a range of about fifty carbohydrates for their creaming action on ammonia latex (Table VI). Numerous simple and substituted



Figure 3
(Magnification, 740 diameters)



Figure 4
(Magnification, 740 diameters)

hexoses and pentoses all gave negative results. One disaccharide only was found capable of causing creaming, an aldobionic acid produced in the degradation of gum arabic. The increased efficiency shown by larger molecules of similar types in promoting creaming was well illustrated by the results obtained with the degradation products of gum arabic. Gum arabic itself did not cream latex, but arabic acid, which is the ash-free material obtained by treatment of a gum arabic dispersion with dilute hydrochloric acid, was a fairly good creaming agent. As one, however, descended the scale of molecular complexity of the breakdown product of the arabic acid molecule to the disaccharide aldobionic acid, so the creaming effects weakened. Pure polysaccharides which creamed latex were mannan from yeast, and lichenin from Iceland moss, which is constitutionally similar to cellulose but of smaller molecular size, and is a gel at 2 per cent concentration in water. Starch, starch dextrin, and xylan did not cream latex, but their methyl derivatives did so. Luteic acid, a synthetic material produced by the action of mold on glucose solution, the unit of whose molecule consists of four galactose residues linked to a malonic acid group, also had some creaming action on latex. In face of these results it did not seem possible to relate the creaming action of a substance with chemical constitution, but the importance of large molecular size and a high capability for hydration was demonstrated.

During the examination of the samples of gum tragacanth referred to previously, it was noted that there appeared to be a rough correlation between high viscosity and creaming power. It has been shown by Bächle (*Kautschuk*, 12, 210, 232 (1936)) that the viscosity of the serum after creaming is about one-half of that of a solution of the creaming agent of the concentration in which it is present in the latex prior to creaming. This indicates adsorption of creaming agent by rubber globules, and high viscosity of creaming agent in solution may therefore perhaps be correlated with capability for adsorption.

The suggestion has often been made that creaming agents are effective because they lead to an aggregation of rubber globules, and the fact that these aggregates have not been observed has been explained by assuming that they are dispersed by diluting the latex for examination under the microscope. Stamberger ("Colloid Chemistry of Rubber," 1939, 30) further suggested that these hypothetical aggregates were the result of the creaming agent being strongly adsorbed by the individual globules, thereby altering their electric charge and allowing them slightly to adhere together. Complete coagulation of the rubber was supposed to be prevented by a hydration layer surrounding the globules as a result of the extremely high affinity of the creaming agents for water. Experimental support for this very reasonable hypothesis, previously lacking, has now been obtained, and it has been demonstrated conclusively that aggregation of the rubber globules does occur when latex is mixed with a creaming agent, that this aggregation leads to cessation of Brownian movement, and that the aggregates are reversible and may be broken up by dilution of the cream with water. These conclusions are based on the results of the following experiments, and are illustrated by the accompanying photographs.

When diluted to about 1 per cent of rubber, preserved latex creamed with tragon seed gum (Fig. 1) showed vigorous Brownian movement, which could in no way be distinguished from that shown by the diluted original latex (Fig. 2). When latex of 2 per cent concentration was mixed with equal volumes of 0.6 per cent tragon seed gum, thereby bringing the concentration of creaming agent to that used in practice (0.3 per cent), Brownian movement was slowed down at once with aggregation of the single globules into clusters, and eventually Brownian movement ceased. The size of the clusters two minutes after mixing is shown in Fig. 3, and



Figure 5
(Magnification, 740 diameters)



Figure 6
(Magnification, 740 diameters)

ten minutes later in Fig. 4. The slide was kept under observation for about an hour, but no further aggregation was observed. The same mixture was allowed to cream in a glass cylinder overnight, and a drop of the shallow cream which had formed was then examined under the microscope (Fig. 5). The clustering effect was still very marked, but perhaps the aggregates of rubber globules were not so compact as those in Figs. 3 and 4. Some of the cream was then diluted with water when Brownian movement recommenced and proceeded undiminished for some hours (Fig. 6). The conditions of the preceding experiment might be criticized as not fairly representing those occurring in practice, for though the amount of creaming agent added is usually 0.3 per cent on the aqueous phase, a proportion is adsorbed on the surface of the rubber globules, so reducing the concentration of creaming agent in the aqueous phase. In very dilute latex, as used for microscopic observation, the total amount adsorbed is obviously much less than occurs under industrial conditions. An experiment was, therefore, made in which latex was diluted to 1 per cent dry rubber content, with the lower layer from latex creamed in the normal way, and immediate aggregation of rubber globules was observed under the microscope. The aggregation that occurs on the addition of creaming agent does not adversely affect the stability of latex to mechanical influences, such as stirring in the presence of zinc oxide. Based on a test of this nature, the stability of a sample of preserved latex was increased by about 60 per cent on the addition of the normal amount of creaming agent. Freundlich has suggested that the creaming agent acts as a "sensitizer," but the above experiment does not support this view. In this connection the curious behavior of saponin with preserved latex is of interest. The use of saponin in low concentrations as a protective colloid for rubber latex is well known, but surprisingly in concentrations of about 10 per cent it is capable of creaming preserved latex.

A creaming agent must therefore be capable of adsorption on the latex particles, and of hydration. These qualities usually go with large molecular size and the ability to form viscous solutions with water, and are shown by other substances than creaming agents, *e. g.*, casein and starch. Starch solution, however, was found to have no diminishing action on the Brownian movement, and it did not cause aggregation of the particles. The ability to cause reversible aggregation of the particles with reduction in Brownian movement, therefore, may be the distinctive property of creaming agents.

The author wishes to acknowledge his indebtedness to the London Advisory Committee for Rubber Research (Ceylon and Malaya) for permission to publish the results of work conducted in their laboratories, to G. Martin and W. S. Davey for their continued interest in the work, and to the latter for his assistance in the preparation of the paper.

The Coagulation of Latices by Polar-Nonpolar Liquids

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I

So many substances have been used as coagulants for latices, particularly for Hevea latex, that it would have been surprising if organic liquids, both soluble and poorly soluble ones, had not been tested. Ethyl alcohol is known as "one of the oldest coagulating media."¹ The amount necessary for coagulating is very large; more than 500 cc. of ethyl alcohol (96 per cent) per liter of undiluted Hevea latex are needed to bring about complete coagulation (in several hours). Hence we are dealing with a marked change of the medium of dispersion. Occasionally experiments have also been made² with liquids not miscible in all proportions with water and aqueous solutions, such as toluene, chloroform, amyl alcohol, etc. The experimental conditions were, however, often not well defined. Such liquids cause the rubber particles to swell after some time (minutes or hours), and the changes caused by the swelling are not always readily distinguished from those due to mere coagulation.

When experimenting with Abiarana gutta-percha latex, we became interested in organic coagulants.³ This latex is not coagulated irreversibly by electrolytes. The only way so far known to coagulate it is to add large amounts, *e. g.*, 80 or more parts of ethyl alcohol or acetone, to 100 parts of diluted latex. Various organic substances soluble in water, such as methyl, propyl, and isopropyl alcohol, ammonium lactate, sodium benzoate, etc., were tested; none was more effective as a coagulant than ethyl alcohol or acetone. On trying, however, a number of organic liquids which are but poorly soluble in water, it seemed that fairly simple and straightforward results might be obtained by using diluted latex, adding so much of the liquid that a second phase is formed and shaking vigorously. With the majority of liquids the stability of Abiarana latex is not affected; after some minutes the two phases separate again unchanged. Several liquids were found, however, which coagulated Abiarana latex completely within a few seconds, producing a lump of gutta-percha which floats mostly at the interface aqueous solution/organic liquid.

Comparing coagulating with non-coagulating liquids, it became obvious that only liquids which are not miscible with water in all proportions, and the molecules of which have a distinctly polar-nonpolar structure, are able to coagulate Abiarana latex in this way. Substances with nonpolar molecules are inactive. By polar-nonpolar structure we mean that the molecules consist of a nonpolar part, such as an alkyl group, and of a polar part, such as hydroxyl, carboxyl, keto, amino, or similar groups, which have a strong affinity to water.

The liquids tested are given in Table I.

The polar-nonpolar liquids mentioned coagulate diluted Abiarana latex mostly very rapidly; some like ethyl acetate and ethyl acetoacetate a little more slowly, *i. e.*, after some 15 to 20 seconds' vigorous shaking.

TABLE I

Nonpolar Substances (No Coagulation)	Polar-Nonpolar Substances (Coagulation)
Petroleum ether	<i>n</i> -Butyl alcohol
Paraffin oil	Isobutyl alcohol
Decalin	<i>n</i> -Amyl alcohol
Carbon tetrachloride	Isoamyl alcohol
Chloroform	Capryl alcohol
Tetrachloroethane	Isobutyric acid
<i>n</i> -Butyl chloride	Valerianic acid
Benzene	Methyl formate
Toluene	Ethyl formate
Cyclohexane	Methyl acetate
Tetralin	Ethyl acetate
Chlorobenzene	Ethyl malonate
α -Bromonaphthalene	Ethyl acetoacetate
Nitrobenzene	Cyclohexanol

Diluted Hevea, Funtumia, and Jelutong latex are also coagulated in this way by the polar-nonpolar liquids mentioned in Table I, whereas they are left unchanged with nonpolar liquids. This does not seem to agree with some earlier results,⁴ probably owing to a difference in the manner of procedure: By shaking vigorously we disperse the organic liquid as rapidly and finely as possible in the latex and allow it to separate as a second phase, when shaking has stopped. During this short process of coagulation the latex particles remain practically unchanged, whereas previous experimenters appear to have left the organic liquid for a long time in touch with the latex, the latter not having been diluted. Then, of course, the swelling of the latex particles (and other processes needing a longer time) may cause changes similar to coagulation in the true sense of the word; in our case coagulation is particularly successful, if the organic liquid separates quickly from the aqueous phase.

II

The coagulation by organic liquids observed in our experiments is probably due to the following mechanism. The latex particles in the latices mentioned are more or less hydrophilic, owing to films of proteins or other substances coating them.⁵ They therefore remain in the aqueous phase and are not accumulated at the interface if the latex is shaken with a nonpolar liquid whose droplets are markedly hydrophobic. If, however, a polar-nonpolar liquid is used, two new factors have to be taken into account:

(a) These liquids are as a rule more soluble in water than nonpolar liquids; hence the dissolved molecules of the organic substance may be adsorbed by the latex particles, thus making them less hydrophilic. These liquids may act like the collectors in the flotation process, which are adsorbed by the particles of the valuable minerals, thus suppressing their tendency to remain in the aqueous phase and favoring the accumulation in the foam,⁶ the latex particles corresponding to these mineral particles. The importance of a certain degree of solubility is exemplified by the fact that polar-nonpolar liquids, which are higher members of a homologous series, are generally not such good coagulants. Moreover, the tendency of the latex particles to swell quickly is greater with these substances. This first point is presumably the most important.

(b) A second point may also be of influence: The interface latex/polar-nonpolar liquid is less hydrophobic than the one towards a nonpolar liquid. The molecules of the polar-nonpolar liquid are probably oriented in part with their hydrophilic

group towards the aqueous phase. Somewhat hydrophilic particles, such as latex particles, may therefore accumulate more easily on the less hydrophobic interface.

In flotation, the mineral particles accumulate in large amounts on the surface of a stable foam. In our case the aim is somewhat different, the latex particles being coagulated, and separated from the second phase, the organic liquid. This takes place when the droplets of the organic liquid unite when shaking stops, the particles being driven together in a layer of the interface, which decreases more and more in size during separation of the two phases. As indicated above, the instability of the emulsion seems to be an important point of this coagulation process. This fits in with the fact that the latex of *Ficus elastica*, stabilized with NH_3 , can also be coagulated by shaking with polar-nonpolar liquids. The process, however, does not work so efficiently as in other cases, because the organic liquid is emulsified in the latex to a fairly stable emulsion. This latex contains a soap-like substance, probably an ammonium salt of a resinic acid, which acts as emulsifier.

III

The coagulation by some of the lower members of the homologous series deserves brief discussion. In the case of ethyl alcohol or acetone, the amount of coagulant necessary is so large that the nature of the medium is strongly altered. The theoretical conceptions of Kruyt' on the hydration and electrical charge of particles in hydrophilic sols may probably be applied here, the presence of electrolytes being of great importance. A few other cases are, however, interesting.

If 5 to 10 per cent of isopropyl alcohol is added to diluted Abiarana latex, the gutta-percha may be coagulated partly, provided that the liquid is vigorously shaken. The mechanism of this process appears to be similar to that discussed above, i. e., on shaking, an unstable foam is formed which acts like the unstable emulsion formed with a polar-nonpolar liquid. The alcohol adsorbed on the latex particles makes them sufficiently hydrophobic to be accumulated to a certain extent on the surface liquid/air, the air bubbles being surrounded by an orientated layer of organic molecules, as are the droplets of the polar-nonpolar liquid. The parallelism to the action of a collector in flotation is still more pronounced than in the cases discussed above. When the foam collapses, the particles are suddenly strongly driven together and thus coagulated. The activity of the air as a second phase is proved by the fact that if the system is moved without producing foam (e. g., by rolling a test tube filled with Abiarana latex + 10 per cent isopropanol (calculated on the diluted latex) quickly to and fro for 15 min.), there is no coagulation. Propanol behaves like isopropanol, but somewhat less strongly.

It is rather surprising on the other hand that butanol and isobutanol behave differently from propanol and isopropanol. The former substances are mentioned in Table I as coagulants when present as a second liquid phase. If, however, concentrations are taken at which butanol and isobutanol are soluble in the aqueous solution (below 12 and 9 per cent, respectively), Abiarana latex is not coagulated by these substances. This is the more anomalous, since one would expect butanol compounds to be better adsorbable on the latex particles than propane derivatives. The decisive point seems to be that the foam formed by butanol and isobutanol is much more stable than that formed by propanol and isopropanol; a stable foam is distinctly disadvantageous to coagulation, because the latter process only takes place if the bubbles collapse or the droplets of an emulsion are unstable, as explained above.

Phenol, though a polar-nonpolar liquid, is an exception to the rule given in Table I. It does not coagulate Abiarana latex, even if present as a second liquid phase.

There are therefore exceptions to the rule. This is probably in part due to the

fact that we have neglected details about the orientation of the polar-nonpolar molecules at the interfaces, a factor of decisive importance.⁸ Unfortunately not enough is known about the actual orientation of the molecules under various circumstances.

It may be open to discussion whether our explanation, based on the orientation of polar-nonpolar molecules, holds quite generally with different kinds of latices. If the particles are coated with protein or some other substance, the polar-nonpolar liquid may produce some other change in the surface layer, a denaturation or coagulation of the protein, for instance, which might also favor the accumulation of particles at the interface of the two liquids.

IV

Jelutong latex provides an example of the manner in which coagulation by organic liquids may differ from that by electrolytes, and may have special advantages. This latex is more a resin than a rubber system. In the sample which we used, 19.85 per cent (*i. e.*, nearly 80 per cent of the total dry content of the latex) consists of resins or resin-like substances. If Jelutong latex is coagulated by acetic acid, a sediment is formed which is sticky and more plastic than elastic.

If, however, Jelutong latex, stabilized with ammonia and not having been in contact with air for any length of time, is shaken vigorously with a suitable polar-nonpolar liquid, *e. g.*, isobutanol, amyl, or isoamyl alcohol, a lump of rubber is formed at the interface of the two liquids. It has excellent elastic properties and contains only very little foreign matter: it contained 21.5 per cent of the total dry matter, the percentage of pure hydrocarbon in the latex being 21.2 per cent.

The resins are dissolved or peptized in the organic solvent. When the latter has been separated from the aqueous phase and the liquid distilled off, the resins are found as a perfectly transparent mass (without any yellow component), insoluble in water, hard, dry, and not at all sticky at room temperature; 65.1 per cent of the total dry matter was obtained as resins.

Since Jelutong latex does not behave as an ampholyte and is only coagulated slowly by acetic acid, coagulation by organic liquids can also be done with an acid latex. The results are not equally good. Coagulation is more rapid, it is true, as is the rule, if the particles are partly discharged. But the coagulum of rubber is less dry and elastic, and it contains more foreign substance (23.9 per cent instead of 21.5 per cent of the total dry content). The amount of resins found in the organic liquid was correspondingly smaller, 62.2 per cent only. Probably resinic acid is formed, on adding acid, from the resin soaps present in the alkaline latex; this resinic acid is less soluble in the aqueous phase than the soaps and is therefore partly precipitated with the rubber.

Summary

(1) Diluted latices—Abiarana gutta-percha latex was specially investigated—may be coagulated by shaking them with organic liquids, not miscible with water in all proportions, provided that the liquids form a second liquid phase and that their molecules have a polar-nonpolar structure (butyl alcohol, isobutyric acid, cyclohexanol, etc.). Nonpolar liquids (petroleum ether, chloroform, etc.) do not coagulate diluted latices on shaking under these conditions.

(2) This coagulating action can be explained by assuming that the latex particles are strongly accumulated at the interfaces of polar-nonpolar liquids and water; this is not the case with nonpolar liquids.

(3) Small concentrations of some polar-nonpolar substances of small molecular weight, soluble in water, can also coagulate Abiarana gutta-percha latex if they

form unstable foams; this was observed with propanol and isopropanol. If the foam formed under these conditions is stable, as with small concentrations of dissolved butanol and isobutanol, no coagulation takes place. This behavior can be explained as in (2), the air bubbles behaving like the second liquid phase.

(4) Jelutong latex is known to contain an excess of resins, compared with the amount of rubber. A method of coagulating this latex quickly and separating the resins from the rubber consists in shaking the latex for some seconds with certain polar-nonpolar liquids, forming a second liquid phase, such as isobutyl or isoamyl alcohol. A lump of rubber is accumulated at the interface of the two liquids; the resins are contained in the organic phase.

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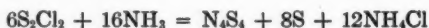
- ¹ O. de Vries, "Estate Rubber," Batavia, 1920, p. 214.
- ² H. Lecomte, *Soc. d'Études Colon.*, 1902, p. 677, reviewed by C. O. Weber in *India Rubber J.*, 26, 19 (1903); Vernet, *Caoutchouc et Gutta-percha*, 17, 10, 193 (1920); de Vries, *Rec. trav. chim.*, 42, 701 (1923); *Arch. Rubbercultuur*, 9, 631 (1925).
- ³ Daniel, Freundlich, and Söllner, *Trans. Faraday Soc.*, 32, 1570 (1936).
- ⁴ Cf. 2. The figures given by Lecomte for the coagulation of Landolphia latex by a series of alcohols—from 100 for methyl alcohol to 9 for amyl alcohol—do not disagree with our results. These figures are not coagulation capacities, but the amounts of alcohol necessary to coagulate the same amount of rubber.
- ⁵ This holds good, for instance, in the case of Abiarana latex, mentioned above.
- ⁶ Cf., for instance, W. Petersen, "Schwimmaufbereitung," Dresden and Leipzig, 1936, p. 134.
- ⁷ Cf. H. R. Kruyt, "Colloids," New York, 1930, p. 197.
- ⁸ Cf. the behavior of collectors in flotation (W. Petersen,⁶) and the importance of orientated adsorption for the swelling of starch and collagen in solutions of organic substances (Katz and collaborators, *Biochem. Z.*, 263, 421 (1933); 271, 54 (1934), and preceding papers). In the latter cases too the influence of phenol on swelling was found to be the reverse of that of all other polar-nonpolar substances.

Highly Reactive Sulfur or the Reaction of Ammonia and Sulfur Chloride in Rubber Solutions

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If a small quantity of sulfur chloride is diluted with a solvent such as petroleum naphtha and ammonia gas is passed through the mixture, the usual precipitate consisting principally of ammonium chloride is formed, according to the usually accepted equation:



The following researches show that, if to the petroleum solution of sulfur chloride a quantity of rubber solution is added, a precipitate does not form on adding of ammonia gas; if, however, the sulfur chloride is increased above a certain percentage, a precipitate again forms on adding ammonia, but this time of an entirely different type.

Sulfur is thus combined with the rubber in a remarkably spontaneous way, and the precipitate contains essentially the rubber sulfur product, a rubber nitrogen sulfide product, a small amount of S_2Cl_2 -rubber additive product, ammonium chloride, free sulfur, and nitrogen sulfides. With the necessary amount of S_2Cl_2 , the rubber-sulfur product may be obtained containing over 32% combined sulfur, which ordinarily requires for its production the heating of mixtures of sulfur and rubber together at high temperatures for long periods.

The researches concern the properties of the precipitate and factors in its formation, with its bearing on essentially rubber chemistry problems. The components of the precipitate of essential interest, *viz.*, the rubber combination products, were extracted by special treatment, and are referred to throughout as "treated precipitates," while the original precipitate, which includes the NH_4Cl , etc., is referred to as "original precipitates."

Reagents

The benzene was a petroleum fraction, of specific gravity 0.68, and a boiling range of 60-110° C. The rubber was ordinary smoked sheet. S_2Cl_2 was added in the form of a 10% solution in benzene. Ammonia gas was 99.99% purity.

Precipitation Methods

Method No. 1.—In this, the precipitation was made by adding the whole of the S_2Cl_2 to the solution of rubber in benzene and immediately passing NH_3 gas through at a definite rate until the whole of the S_2Cl_2 had reacted up to 5 minutes being required.

Method No. 2.—In this, the concentration of sulfur chloride in the solution was kept very low with the object of ensuring that when high percentages of S_2Cl_2 were used, its direct action on the rubber was kept at a minimum. The S_2Cl_2 was added

in lots of 0.15 gram units, and the NH_3 inflow controlled so that an excess of an approximate "mean" of 0.1 gram of S_2Cl_2 was maintained. The rate of NH_3 was 4 cc. per second, the time of entry about 3 minutes per gram of S_2Cl_2 . The depth of the solution was 7 cm., which was therefore the length of passage of the NH_3 bubble. The diameter of the latter was 9 mm. at release. The temperature of tests was from 20° to 25° C.

Preparation of "Treated Precipitate"

Two methods were used:

Method A. (*Sodium hydroxide treatment.*)—In this method, the ammonium chloride, nitrides, and free sulfur were separated from the "original precipitate" with NaOH solution, and were used for all types of product, *i. e.*, those with high or low sulfur. Some sulfur that must be regarded as "combined," as stated in Method B, is unavoidably removed by this method, the highest percentage of sulfur obtained being 27.2%.

The precipitate, after washing with benzine, was well triturated with a few ml. of aqueous ammonia and NaOH to destroy free nitrogen sulfides still held in the precipitate, and was then dried to a few per cent of solvent at no higher than 150° F. The residue, after washing from NaOH, was sheeted out very thin to 0.075 mm. when of the soft rubber type (low sulfur content); or, when friable (high sulfur content), was crushed, using alcohol for wetting, to an impalpable powder to go through a standard wire sieve of 80 holes to the linear centimeter. This procedure was necessary to remove NH_4Cl . The product, in either case, was then boiled in 5% sodium hydroxide for 2 hours, then in 5% acetic acid, and successive lots of water; after washing in alcohol it was dried at 95° C.

Method B. (*Extraction with water to remove NH_4Cl , etc., and with acetone to remove free sulfur and residual nitrides.*)—This method was confined to high sulfur content precipitates. The sulfur remaining in this product conforms to "combined" as determined by standard methods of acetone extraction.

The whole product was shaken with 50 cc. of water to aggregate the precipitate and settle rapidly. The latter was separated and washed by decantation with benzine, and then boiled with 50 cc. of acetone. Without drying the precipitate residue, it was reduced to an impalpable powder, as in Method A.

NH_4Cl , etc., was then completely removed by boiling in 3% acetic acid and successive lots of water. The residue was transferred to a filter thimble and extracted with acetone. The acetone containing water after an hour's extraction was replaced with a fresh lot, and extraction was continued for 60 hours in a standard extraction apparatus.

Physical Properties

In physical properties, the "original" precipitates—whenever referred to as such—were bulky and gelatinous with the lower amounts of S_2Cl_2 , but nevertheless sharply defined from the supernatant liquid. This gelatinous character changed to flocculent and granular with higher percentages of S_2Cl_2 .

The "treated" precipitate varied from the stage of soft elastic properties of ordinary vulcanizates to that of ebonite powder, this change corresponding to the increase in the sulfur chloride used, and therefore as will be seen to the combined sulfur.

Chemical Properties and Composition

These experiments were carried out on the product of precipitation from Method No. 2, which ensured the minimum of S_2Cl_2 direct-action product. Treatment was

done by Method B, which therefore included all sulfur insoluble in 60 hours' extraction in acetone.

The S_2Cl_2 used was 3 grams (this amount was found to have the optimum effect), rubber 0.4 gram, and the total benzine, including that as 10 per cent S_2Cl_2 solution, 130 grams.

Thirty grams of rubber were masticated for 30 minutes on a 14-inch mill to obtain as granular a precipitate as possible and to ensure the maximum amount of action on the rubber.

The Carius bomb method was used for sulfur estimations.

Results of Analysis: Considerable variation was evident in the yield of treated precipitate and sulfur content.

One set of 3 lots averaged 0.628 gram and showed on analysis—sulfur 33.8%, chlorine 0.53%, nitrogen 2.17%.

Another 3 lots averaged 0.619 gram, giving total sulfur 30.8%, chlorine 0.6%, nitrogen 2.5%.

Still another 3 lots yielded an average of 0.705 gram of precipitate, giving on analysis: sulfur 39.2%, chlorine 0.7%, nitrogen 2.8%.

Extraction in acetone for an additional 40 hours removed only 1.5 per cent extract—mainly nitrogen sulfide—from the last mentioned.

Assuming 0.38 gram of rubber hydrocarbon in 0.4 gram of crude rubber and that the proteins are removed during "treatment," there remains an undetermined amount of substance as high as 6 per cent, which is probably a product of reaction with the solvent and the S_2Cl_2 , or of oxidation.

Treatment with NaOH solutions gave very important results. Boiled for 6 hours in 10 per cent NaOH solution, one lot of 0.69 gram of precipitate containing 39.1 per cent of sulfur as S and N_4S_4 was reduced to 0.568 gram, containing 28.4 per cent sulfur; boiled for a further 44 hours it was reduced to 0.45 gram containing 12.4 per cent sulfur. Thus, it will be seen that this product, produced from this amount of S_2Cl_2 and resembling in properties ordinary ebonite, decomposed in 10 per cent NaOH, the sulfur being extracted progressively.

Normal alcoholic sodium hydroxide had a much more rapid effect, 6 hours' boiling reducing 0.61 gram to 0.47 gram.

Various Factors in the Formation of Precipitate

From a series of tests, it was found there was an exponential increase in "treated" precipitate with concentration in S_2Cl_2 ; and also with concentration of S_2Cl_2 and rubber, *i. e.*, reduction in solvent. The percentage of sulfur increased with this increase in the "treated" precipitate, but it was not determined whether the ratio was constant under all conditions.

Free Ammonia and Rate of Inflow

The rate of inflow of the ammonia gas considerably affected the amount of precipitate formed, the amount being reduced as this rate increased. Complete reaction with the rubber was affected with S_2Cl_2 , in the ratio of 4.5 to 2.6 using a rate of 6 cc. per second of NH_3 , and 0.5 cc. per second, respectively, with Method of Precipitation 1.

Also, when the solution was first saturated with NH_3 and an excess of the latter maintained, adding the S_2Cl_2 in small portions, a precipitate still formed, but in reduced quantities—with the one given amount of S_2Cl_2 —from that when a small excess of S_2Cl_2 was maintained as in Method of Precipitation 2.

Therefore it appears that the amount of precipitate varies, for a constant amount of S_2Cl_2 , inversely with the free ammonia content of the solution.

Direct Action of Sulfur Monochloride

It was proved that the presence of rubber during the actual reaction of the sulfur chloride and the ammonia is necessary for the formation of the rubber precipitate. The product of NH_3 and S_2Cl_2 in benzine contained some active accelerating and vulcanizing component, due apparently to the N_4S_4 contents, but when added to the rubber solution, prolonged heating only produced a vulcanizate containing 2.5 per cent sulfur—probably as N_4S_4 ; which compares with over 30 per cent combined S from the same proportions of these reactants when the rubber was present during precipitation.

The precipitate is not formed directly as a result of the direct action of S_2Cl_2 on the rubber, as shown by the small percentage of chlorine in the precipitate, and by the fact that the precipitate is formed in solutions of alkaline condition. In addition to this, and presuming the possibility of the S_2Cl_2 product being first formed and subsequently decomposed, the S_2Cl_2 was added to the rubber solution in the proportions necessary to produce an ebonite as above, and, after standing, without passing NH_3 , was shaken up with NaOH to neutralize the S_2Cl_2 . The rubber on drying out was found to be soft, tacky, and readily soluble. Consequently, very little, if any, attachment of the S_2Cl_2 to the rubber had taken place.

Mastication had some effect, and the results warrant more investigation.

Sulfur in the precipitate phase was found higher than that in the supernatant liquid. Also the total combined sulfur varied in an inverse manner to the rate of NH_3 entry (Method of Precipitation No. 1).

The Effect of the Reaction on Oils Results in the Formation of Brown Factice

Samples of brown factice or oil substitute can be produced which ordinarily require high temperatures for long periods on a mixture of oil and sulfur. Thus on adding 7 cc. of S_2Cl_2 to 45 cc. of linseed oil and 40 ml. of benzine and then passing NH_3 through, the charge changed rapidly at a certain point, and with evolution of much heat, into a rather soft brown factice, the final stage of the reaction to a hard condition being prevented by the inability to continue the introduction of the ammonia.

Summary of Results and Observations

When sulfur chloride and ammonia gas react in the presence of rubber in a benzine solution, a precipitate is formed which contains, in addition to NH_4Cl , sulfur, etc., sulfur combined with the rubber in varying proportions according to the amount of S_2Cl_2 used and thus the amount of this active form of sulfur produced. A limit is reached, however, beyond which no additional rubber-sulfur product is obtained.

The sulfur in the precipitate is classifiable into:

- (a) uncombined, and soluble in acetone and NaOH solutions.
- (b) combined with the rubber, not extractable with acetone on extraction for standard periods of time of 8 hours for soft vulcanizates to 60 hours for ebonites, but slowly extractable with 10 per cent NaOH solutions.
- (c) present in the precipitate as S_2Cl_2 additive product and as nitride.

As much as 39.5 per cent of (b) plus (c) was obtained, the product in such case resembling ordinary ebonite. The nitrogen content in this case was 2.8 per cent, equivalent to 9.2 per cent N_4S_4 , and the S_2Cl_2 as the additive rubber product was 1.52 per cent. These figures were the highest obtained in any precipitate. Nitrogen was fairly constant between 2.17 and 2.8 per cent for ebonites, and obviously occurred in accordance with some law of equilibrium.

A precipitate containing 39.1 per cent of (b) and (c) was reduced progressively down to 12.4 per cent total sulfur by boiling for a total of 50 hours in 10 per cent NaOH.

All degrees of vulcanizates, containing corresponding amounts of sulfur, were obtained.

Apparently, the sulfur of the reaction combines with the rubber in such a remarkably rapid manner, by reason of its production in a highly active state, and unless contact with the rubber takes place at its formation, it polymerizes and no combination results.

The amount of rubber-sulfur product varies in an inverse manner to the amount of ammonia present in the solution at the time of precipitation. Apparently, this excess NH_3 acts mainly as a preventive of the sulfur reaching the rubber while in its active state.

The full effects of mastication were not determined.

The reaction takes effect on oils, with formation of brown substitute or factice.

The results are of general interest from the standpoint of chemical reaction and physico-chemical effects. They are of importance in regard to problems of vulcanization and the production of vulcanizates, and provide another avenue of investigation for the solution of the various problems relative to these phenomena.

The Mechanism of the Action of Vulcanization Accelerators

Derivatives of Mercaptobenzothiazole. II. The Transformation of Mercaptobenzothiazyl Sulfide

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In the previous communication, dealing with the mechanism of the accelerating action of benzothiazyl disulfide, it was shown that the acceleration of rubber vulcanization in the presence of this agent and of esters of mercaptobenzothiazole is due to a great extent to the formation of mercaptobenzothiazole and its zinc salt.¹ An analogous situation has been observed in the vulcanization of rubber mixtures in the presence of mercaptobenzothiazyl sulfide, although the latter differs in its chemical properties from the compounds mentioned above.

It is well known that esters of mercaptobenzothiazole are chemically less stable than mercaptobenzothiazyl sulfide. They are saponified by the action of alkalies, with the formation of free mercaptobenzothiazole and the acid salts. The esters of polynitrophenols also are easily saponified.

Benzothiazyl disulfide is decomposed by the action of alkalies, with formation of the corresponding alkali salts. It is rather easily reduced to mercaptobenzothiazole.

In contrast to these compounds, mercaptobenzothiazyl sulfide is a highly stable compound. It gives none of the above reactions. Nevertheless, it accelerates the vulcanization of rubber, not only because of the general reasons explained above but particularly because mercaptobenzothiazole and its zinc salt are formed.

The transformation of mercaptobenzothiazyl sulfide to mercaptobenzothiazole is confirmed by the fact that the latter is always formed in the vulcanization of rubber mixtures containing sulfur, zinc oxide, and mercaptobenzothiazyl sulfide. Furthermore, examination of the acetone extracts always reveals the presence not only of mercaptobenzothiazole, but of its zinc salt.

These facts indicate that mercaptobenzothiazyl sulfide, as well as other derivatives of mercaptobenzothiazole in which the mercapto group—SH is blocked, evidently do not themselves accelerate vulcanization. This function is performed by other compounds, *viz.*, the products of the transformation of mercaptobenzothiazyl sulfide formed in the process of vulcanization. Among these decomposition products are mercaptobenzothiazole and its zinc salt, which have been mentioned above.

The importance of these decomposition products as factors of the acceleration of vulcanization is, without doubt, very great. Particularly great is their importance when the derivatives of mercaptobenzothiazole are rapidly decomposed at the temperature of vulcanization, with immediate formation of mercaptobenzothiazole.

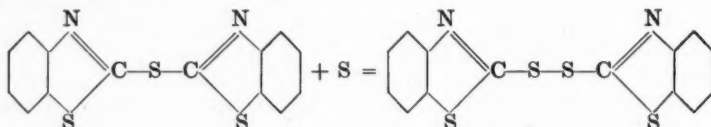
The latter condition, *i. e.*, the rapid cleavage of these substances, is important primarily from the technical viewpoint. Experiments have shown that the more rapid their transformation into mercaptobenzothiazole, the more complete is the process of vulcanization. Conversely, the slower their decomposition, the less complete is the process of vulcanization.

According to the results of previous experimental investigation, benzothiazyl disulfide and certain esters of mercaptobenzothiazole are converted into mercaptobenzothiazole at a sufficiently rapid rate. In the case of mercaptobenzothiazyl sulfide, this conversion is slow, and is besides of a rather complex nature.

This transformation proceeds in the following manner: As the result of the interaction between mercaptobenzothiazyl sulfide and sulfur, unstable addition products² are formed and on heating these combine with the formation of benzothiazyl disulfide.

The soundness of these postulates was confirmed by the following experimental results in an investigation of the reactivity of mercaptobenzothiazyl sulfide. It was found that, on heating with sulfur, the latter reacts, with the formation of benzothiazyl disulfide as the chief product.

The formation of dibenzothiazyl disulfide can be schematically represented by the following equation:

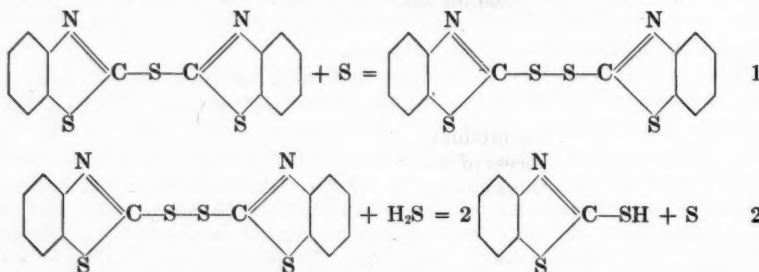


In our opinion the same reaction takes place in the vulcanization of rubber.

The function of the benzothiazyl disulfide formed as a result of this reaction has been explained in the previous communication.

It was then shown that "benzothiazyl disulfide is decomposed in the process of vulcanization of rubber. It is reduced chiefly to mercaptobenzothiazole. The reduction of benzothiazyl disulfide takes place as the result of its interaction with substances capable of cleaving hydrogen atoms. Such substances, under the conditions of vulcanization, can be hydrogen sulfide, formed by the interaction of sulfur with the admixtures of rubber, and, possibly, the hydrogen of the rubber hydrocarbon.³ Moreover, reduction of benzothiazyl disulfide to mercaptobenzothiazole takes place also under the influence of substances of basic character."

By assuming one of these reactions, *viz.*, that of the interaction of benzothiazyl disulfide with hydrogen sulfide, the transformation of mercaptobenzothiazyl sulfide to mercaptobenzothiazole can be represented by the following scheme:



The mercaptobenzothiazole reacts partially with the zinc compounds, forming the zinc salt.⁴

The sulfur, mercaptobenzothiazole, and the zinc salt of the latter formed in the above reaction, are the factors influencing the acceleration of the vulcanization.

It was of interest to inquire into the second aspect of the question relating to mercaptobenzothiazyl sulfide, *viz.*, its practical accelerating activity.

The experiments described below show that mercaptobenzothiazyl sulfide is a feeble accelerator. Rubber mixtures are vulcanized by its action very slowly.

Such behavior in the group of derivatives of mercaptobenzothiazole is very rare.

The question therefore arises as to the cause of this property of mercaptobenzothiazyl sulfide.

From the point of view mentioned above regarding the nature of the action of mercaptobenzothiazyl sulfide, it is evident that in a rubber mixture the latter reacts with sulfur very slowly (Formula 1). Since the subsequent reactions proceed from the first reaction (1), it follows that vulcanization progresses sluggishly.

That the interaction between mercaptobenzothiazyl sulfide and sulfur proceeds slowly is substantiated by the experimental observation that after a prolonged period of vulcanization of rubber compounds, part of the mercaptobenzothiazyl sulfide remains unchanged.

This is further confirmed by the experiments described below, which show that mercaptobenzothiazyl sulfide reacts with sulfur slowly even at elevated temperatures.

Experimental Part

1. *Preparation of Rubber Mixtures. Investigation of the Acetone Extracts.*—Mercaptobenzothiazyl sulfide, used as an accelerator of vulcanization, was prepared by our previous method.⁵ The resulting product was recrystallized twice from methyl alcohol. The recrystallized product melted at 102–104° C.

The rubber mixtures containing mercaptobenzothiazyl sulfide were prepared on a laboratory mill.

The rubber samples were vulcanized in a hydraulic press in molds (2 × 150 × 150 cm.) at a steam pressure of 3 atmospheres.

Samples 1 and 2 were analyzed chemically.

TABLE I
COMPOSITION OF RUBBER MIXTURES

	I	II	III
Smoked sheet	100	100	50
Sulfur	3	2.5	1.5
Zinc oxide	5	5	..
Mercaptobenzothiazyl sulfide	1	1.5	1

The investigation was carried out as follows:

Mixtures I and II were vulcanized and then shredded on rolls and extracted with acetone in a Soxhlet apparatus for 10 hours. The acetone was distilled off on a water bath, first at atmospheric pressure and then at reduced pressure.

The distillation residue of the acetone extraction was dissolved in 50 cc. of grain alcohol, the solution was filtered, and the small fraction of undissolved residue was washed with 10 cc. of alcohol. After distilling the alcohol, the residue was dissolved in boiling benzene. The solution on standing formed a crystalline precipitate. The yellow prismatic crystals had a bitter taste, were difficultly soluble in water, and were fairly soluble in alkali and potassium carbonate solutions. By acidification of the alkaline solution with hydrochloric acid, the product again separated in the form of a flocculent white precipitate. In these properties and in its melting point of 174° C. it was identical with mercaptobenzothiazole. It gave no depression of the melting point in mixtures with mercaptobenzothiazole.

The proportions of mercaptobenzothiazole extracted from these rubber mixtures are shown in Table II.

In addition to mercaptobenzothiazole, the concentrated benzene solution precipitated mercaptobenzothiazyl sulfide. Since the former was less soluble than the latter, the separation was easily effected from dilute benzene solutions.

The fraction of acetone extract insoluble in alcohol proved to contain a little of the zinc salt of mercaptobenzothiazole.

TABLE II

	I	II	III
Extracted rubber mixture (grams)	80	86	39
Isolated mercaptobenzothiazole (grams)	0.15	0.23	0.12

2. *The Reaction between Mercaptobenzothiazyl Sulfide and Sulfur.*—The interaction of mercaptobenzothiazyl sulfide and sulfur was studied under the following conditions.

Equimolecular parts of mercaptobenzothiazyl sulfide and sulfur were thoroughly mixed in a porcelain mortar. The mixture was then transferred to a glass flask, which was immersed in a heated oil bath below the level of the contents.

At 100–115° C. of the oil bath, the contents of the flask began to melt, and on further heating to 120–125° C. formed a brown liquid mass. The temperature was then raised to 155–160° C. and held at this range for 1–3 hours, depending on the quantities of the components used in the reaction. After completion of the reaction, the fused mass was dissolved in boiling benzene and then filtered. The solution on standing at room temperature precipitated benzothiazyl disulfide as white, glistening scales. After recrystallization the product melted at 179–180° C.

TABLE III

RESULTS OF THE REACTION BETWEEN MERCAPTOBENZOTHAZYL SULFIDE AND SULFUR

	Reaction Components (Grams)			
	Mercaptobenzothiazyl Sulfide	Sulfur	Yield of Benzothiazyl Disulfide	Melting Temp. (° C.)
(1)	1	0.1066	0.74	179–80°
(2)	1	0.107	0.78	179–80°
(3)	1	0.107	0.81	179–80°

Analysis of $C_{11}H_8N_2S_4$. Calcd.: N 8.42, S 38.6%; found: N 8.66, S 38.7%.

Conclusions

1. During the vulcanization of rubber, mercaptobenzothiazyl sulfide is transformed into mercaptobenzothiazole and the zinc salt of the latter.

2. This transformation is effected by the interaction of mercaptobenzothiazyl sulfide with sulfur. As a result of this reaction unstable products of addition of sulfur and mercaptobenzothiazyl sulfide are formed, and when heated these are converted into benzothiazyl disulfide.

3. During vulcanization, benzothiazyl disulfide decomposes into mercaptobenzothiazole and the zinc salt of the latter.

4. The acceleration of vulcanization of rubber by mercaptobenzothiazyl sulfide, as well as by other derivatives of mercaptobenzothiazole in which the mercapto—SH group is substituted, is attributable to several causes, the chief of which is the formation of mercaptobenzothiazole and its zinc salt.

References

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- 5 Zelde and Petrov, U. S. S. R. Pat. No. 40,564.

The Effect of Organic Accelerators on the Temperature Coefficient of Vulcanization

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During the last decade innumerable organic accelerators have been developed, and it has become possible to reduce the time of vulcanization to a few minutes. The main difficulty encountered with these ultra- or super-accelerators is their liability to prevulcanize rubber on the compounding mill, thus rendering the masticated stock more or less useless for further processing.

This led to the development and marketing of so-called "high critical temperature" and "delayed action" accelerators. The former have been considered safe below a certain temperature, whereas the latter exhibit a time-lag which allows for mixing and compounding on the mill without risk of scorching. The explanation of the action of "high critical temperature" accelerators is that they consist of two inactive ingredients, which, when heated to vulcanizing temperatures, react, producing an ultra-accelerator. Delayed action, on the other hand, is generally effected by the hydrolysis of an inactive ester of the active accelerator with certain acids or bases, as the case may be.

It has been suggested, however, that both the above-mentioned properties are usually co-existent with one another, and the present investigation has been mainly undertaken to determine whether commercial accelerators of the "delayed action" type actually show a critical temperature.

If accelerators have a critical temperature, as suggested, then the temperature coefficient of vulcanization must vary definitely around the critical temperature, and cannot possibly be a constant. The temperature coefficient of vulcanization is defined as the factor with which the time of cure must be multiplied if the temperature of vulcanization is lowered by $10^{\circ}\text{C}.$, in order to effect the same state of cure. Thus it is a ratio of times, and its numerical value does not give any indication about the speed of vulcanization itself. It should not be confused with the coefficient of vulcanization.

Historical Survey

Temperature coefficients of various accelerators have been determined recently and the values reported are summarized in the table on the following page.

These temperature coefficients have been found to be constants over the whole range of investigation, which in Sandstrom's case reached down to $90^{\circ}\text{C}.$ This means that none of these accelerators showed signs of a critical temperature.

It may further be seen from the table that there are two different ways of evaluating the temperature coefficient, giving two different results. One is by means of the physical changes during vulcanization, *i. e.*, by comparison of modulus figures; the other is by determining and comparing the amounts of sulfur chemically combined with the rubber. In either case it is assumed that two or more vulcanizates with identical moduli or identical percentages of combined sulfur, respectively, have reached the same state of cure, and on this assumption the evaluation of the respective temperature coefficient is based.

Accelerator	Temperature Coefficient		Investigator
	Determination from Modulus	Combined Sulfur	
Mercaptobenzothiazole	1.91	2.30	Park and Maxwell (<i>Ind. Eng. Chem.</i> , 24, 148 (1932)).
Crotonaldehydeaniline	2.32	2.67	
Tetramethylthiuram disulfide	1.92	2.20	Sandstrom (<i>Ind. Eng. Chem.</i> , 25, 684 (1933)).
Butyraldehydeaniline condensation product	2.52	2.40	
Benzothiazyl disulfide	2.00	2.08	Morris (<i>Ind. Eng. Chem.</i> , 25, 1402 (1933)).
Mercaptobenzothiazole	1.82	2.11	
Zinc dimethyldithiocarbamate	1.98	2.06	

How is it possible, however, to explain the discrepancy between the two results obtained by the above-mentioned methods from one accelerator? Park and Maxwell, for example, find for mercaptobenzothiazole temperature coefficients of vulcanization of 1.91 and 2.30 by the physical and chemical methods, respectively. If a mercaptobenzothiazole stock is cured at 150° C. to a definite physical state, *e. g.*, the physical optimum, it may be assumed that the percentage of combined sulfur is about 2 per cent. If now vulcanization is effected at 140° C., then to obtain the physical optimum the period of vulcanization must be increased 1.91 times, but to obtain the same percentage of combined sulfur, the period of vulcanization must be increased 2.30 times. With a period of vulcanization of 1.91 times the original required at 150° C., the optimum physical properties are obtained at 140° C., but the combined sulfur is only $2 \times \frac{1.91}{2.30}$ per cent. It similarly follows that a vulcanization temperature of 100° C. requires (1.91)⁵ times the original vulcanization period to give optimum properties, but that in this case the combined sulfur is now only $2 \times \left(\frac{1.91}{2.30}\right)^5$ or 0.88 per cent, a figure which is incompatible with known facts.

Seidl (*Gummi-Ztg.*, 34, 797 (1920)) advanced an explanation for this divergence in physical and chemical behavior, stating that the shorter the time of vulcanization the higher is the tensile strength corresponding to a definite combined sulfur content. Shepard and Krall (*Ind. Eng. Chem.*, 14, 951 (1922)) subsequently came to the conclusion that the percentage of combined sulfur and the physical state of a vulcanizate could not be proportionally related to each other.

Of the two methods mentioned above for the evaluation of a temperature coefficient, the author has felt justified, as did Park and Maxwell (*loc. cit.*) in rejecting the combined sulfur method. No investigation has yet disclosed the exact action of sulfur during vulcanization, either in the presence or absence of accelerators, and from a technical point of view modulus is of greater significance than the amount of combined sulfur.

Experimental Procedure

A base mixture consisting of pale crepe rubber 100, zinc oxide 5, stearic acid 1, sulfur 2.5 parts by weight, was prepared, divided into four parts, and 1 per cent of the accelerators diphenylguanidine, Vulcafor D. A., Ureka, and Ureka White, respectively, added to each part. The stocks were then cured in an ordinary treble-daylight press, the temperature of which was controlled by an automatic free-vane controller. Each stock was vulcanized in disc form at 110°, 115°, 120°, 125°, 130°, 135°, 140°, 145°, 150°, 155°, 160°, 165°, 170°, 175°, 180°, 185°, 190°, 195°, 200°, 205°, 210°, 215°, 220°, 225°, 230°, 235°, 240°, 245°, 250°, 255°, 260°, 265°, 270°, 275°, 280°, 285°, 290°, 295°, 300°.

130°, 135°, 140°, 145°, and 150° C. for three different times, which were carefully checked by a stop-watch. In order to reduce possible errors introduced by the low heat conductivity of rubber, the discs were cured 1 mm. thick, instead of the usual 3.0 mm. Ordinary Schopper rings were then cut, and the modulus tested by measuring the weight necessary to elongate the rings to 400 per cent of their original length. Instead of taking the average thickness of the rings, which constitutes another source of errors, they were weighed accurately to 0.005 gram. All rings weighed from 0.85 to 1.3 gram; 1 gram was taken as standard, and all moduli corrected to that weight in the usual way. These corrected moduli were then diagrammatically plotted against time of cure, and nine different lines thus

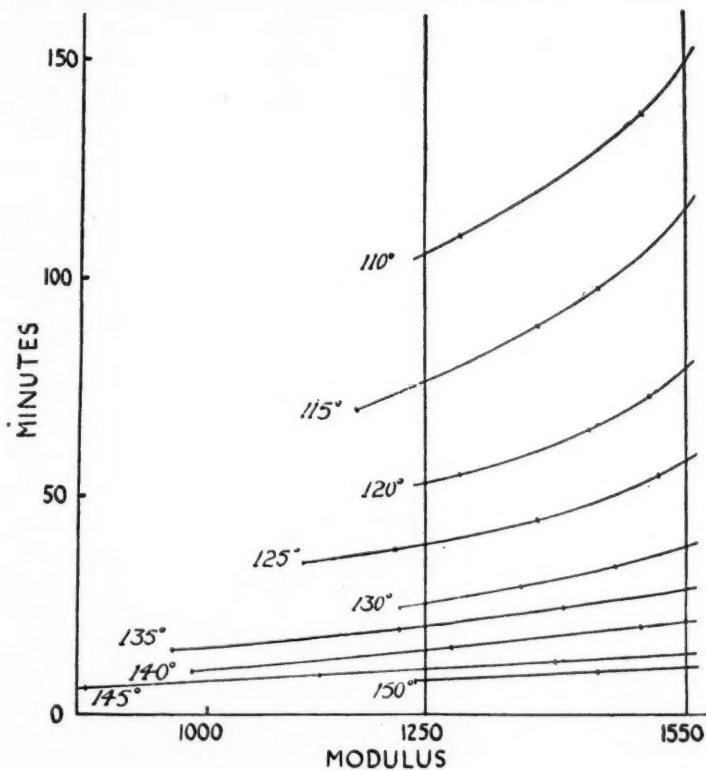


Figure 1

obtained for every accelerator, showing the change in modulus with time of vulcanization at the nine different temperatures. By comparing the times necessary at different temperatures to produce vulcanizates of identical modulus, the temperature coefficient of vulcanization for the whole range tested was obtained. The results, however, were very conflicting, and gave in all four cases such widely varying temperature coefficients as to be useless.

Improved Technic and Results

After a detailed search for the source of error, it was finally found to have originated from differences in temperature of parts of the press. Though the controlling

thermometer could be relied on, it actually only controlled a small part of the press. This was clearly shown when an ordinary stock containing mercaptobenzothiazole was cured for the same length of time in 60 different parts of the press, and the modulus tested as before. The moduli thus obtained gave a variation of as much as 13 per cent in the results.

In order to eliminate this error the press was shrouded with asbestos curtains 1 inch thick, and small steam traps were fitted to each platen, apart from the ordi-

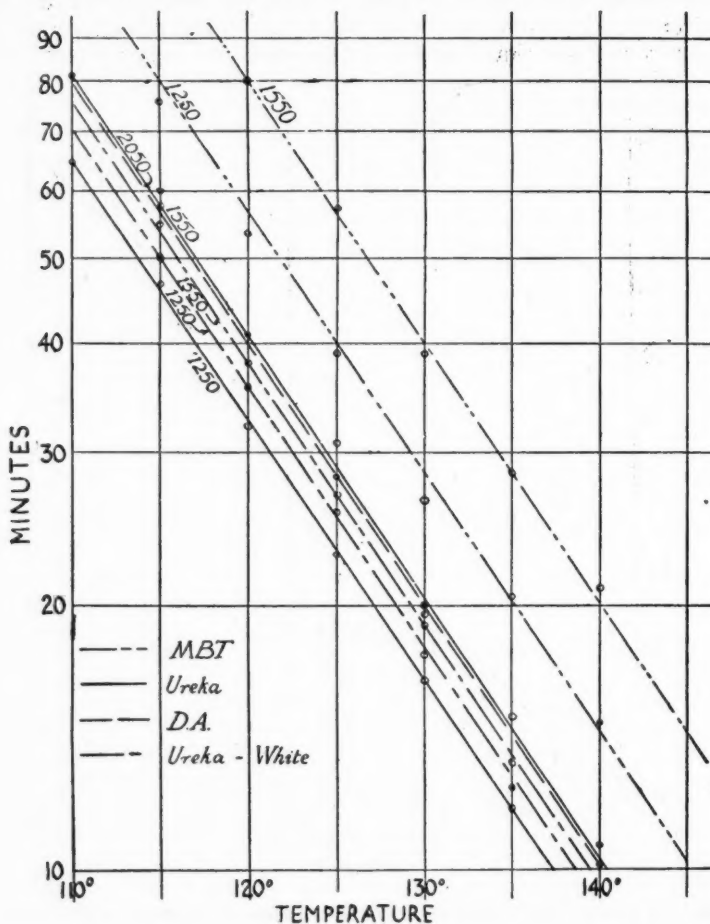


Figure 2

nary main steam outlet trap. Six further discs were then cured near the middle of the center platen around the controlling thermometer, and the same stock was vulcanized to a lower modulus in order to exaggerate possible deviations. The maximum discrepancy was found thus to have decreased to 0.5 per cent.

Four stocks, the composition of which was as given in the previous part, were now prepared, and the accelerators mercaptobenzothiazole, Ureka, Ureka White, and Vulcafor D. A. were incorporated, the last three being "delayed action"

accelerators and the first one a simple accelerator of similar activity, but without delayed action. In this case all cures were made at the six checked and marked positions of the center platen of the press. Moduli were then tested and corrected exactly as described before, and plotted against the time of vulcanization. Four diagrams were thus obtained, all similar in character, of which the one for mercaptobenzothiazole is given in Fig. 1 as an example.

In the case of mercaptobenzothiazole, Ureka, and Ureka White, the times necessary to produce stocks with the moduli 1250 and 1550 were read from the diagram. Thus two independent sets of figures were obtained, each set representing times necessary to produce an identical state of cure. By plotting the logs of these times against temperature of vulcanization, straight lines were obtained, indicating constant temperature coefficients and the slopes of all were found to be exactly two. In the case of Vulcafor D. A. the moduli obtained were higher, and therefore the modulus of 2050 was chosen as average. Here again the result was a constant temperature coefficient of two (see Fig. 2).

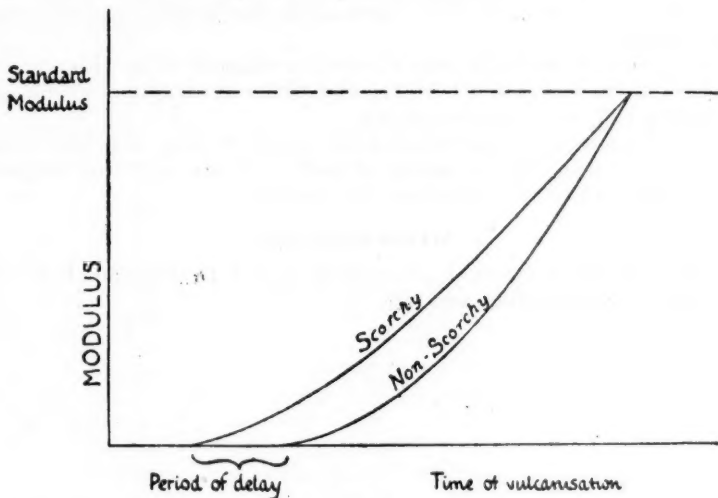


Figure 3

Discussion of Results

This investigation on the activity of three well-known "delayed action" accelerators shows definitely that their temperature coefficients are constant and identical. The constancy proves that for as low a temperature as 110°C . no sign of a temperature limit is distinguishable, below which the stock in question would either not vulcanize or would take abnormally long to cure. The identity shows that, if the stocks are once cured to a fairly high modulus, there is no means of distinguishing between the change in activities of ordinary and delayed-action accelerators with change in temperature. The difference in action can only be observed at the incipient vulcanization, *i. e.*, when very low moduli only are reached.

At whatever temperature vulcanization takes place, "scorchy" and the "non-scorchy" accelerators of the same activity need the same time to produce a vulcanizate of reasonable modulus, but the manner in which this state of cure is reached may be distinctly different, as shown in Fig. 3.

This conception is compatible with the assumption that delayed-action accelerators consist of an inactive ester which hydrolyzes under the influence of heat, producing an active accelerator. According to chemical laws this hydrolysis should take place over an extremely wide range of temperatures, and its own speed of reaction is controlled by its own constant temperature coefficient.

As it has been proved that the temperature coefficient of vulcanization of the resulting active accelerator is constant, it follows that the period of delay occupies a constant proportion of the whole curing time, at whatever temperature within this range the vulcanization takes place.

Conclusions

(1) The temperature coefficient of vulcanization to a standard modulus is 2.0 in the presence of mercaptobenzothiazole, Ureka, Ureka White, and Vulcafor D. A.

(2) The temperature coefficients of vulcanization in the presence of all accelerators tested, including those of delayed action type, are constant over a wide temperature range (110–150° C.). None of the accelerators appears to have a critical temperature.

(3) Differences between the rates at which modulus develops with accelerators of similar activity may account for the fact that some induce scorching on the compounding mill, whereas others do not.

(4) At all temperatures investigated, the period of delay of a delayed action accelerator may represent a constant proportion of the total time required to reach a definite state of cure, as indicated by modulus.

Acknowledgments

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Mechanism of Rubber Vulcanization with Sulfur

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THAT vulcanization of rubber with sulfur always involves a chemical reaction consisting in the addition of sulfur to the double bonds of the rubber molecule has been conclusively established (18, 28). The facts indicate that this addition of sulfur to rubber is an irreversible reaction (31). The temperature coefficient of the reaction is high, increasing about 2.65 fold per 10° C. at ordinary curing temperatures (31). Furthermore, the reaction is apparently exothermic (4, 24). It is noteworthy that catalysts are apparently necessary, since synthetic rubbers prepared from pure materials add sulfur slowly, if at all. The proteins and perhaps the resins in natural rubber undoubtedly serve as accelerators.

The curves for combined sulfur *vs.* time of cure for typical mixes are shown in Figures 1 and 2. Figure 1 is taken from the data of Kratz and Flower (16); the composition and temperature of cure for this mix are shown in Cranor's Table I (9). Figure 2, curve 1, is from Table I of Eaton and Day (10), and curve 2 from data obtained in this laboratory (27, Table I). Superficial inspection of these curves shows extraordinary divergence of type. Figure 1 is a typical fade-away curve, characteristic of most chemical reactions, where the reaction rate decreases with decreasing concentration of the reacting materials. Curve 1, Figure 2, is an entirely different type, where the rate of sulfur addition is constant until nearly 70 per cent of the initial sulfur has reacted. Curve 2, Figure 2, shows even more complex behavior. Again the rate is constant in the initial portions of the cure. However, following this period, the rate increases markedly but later falls off, approaching zero, to give an S-shaped curve.

Experience shows that sulfur combination curves of the type given in Figure 1 are obtained, in general, with accelerated mixes of low initial sulfur. Curves similar to No. 1, Figure 2, are obtained with intermediate sulfurs and those resembling No. 2 with high initial sulfurs.

All these facts must be fully explained by any adequate theory of the mechanism of vulcanization. Nordlander (22) considered only the earlier portions of sulfur combination curves of the type of curve 1, Figure 2, and was led to believe that the reaction was of zero order; that is, the rate

was independent of concentration of the reacting materials. However, the line always eventually develops curvature and the combined sulfur approaches the value of the initial sulfur asymptotically. These facts were neglected by Nordlander. Blake (4), considering the high-temperature, high-sulfur data of Glancy, Wright, and Oon (12) and using an empirical time correction, found that the reaction was apparently second order. However, Blake's method cannot be applied to mixes of other compositions and other temperatures such, for example, as shown in curve 2, Figure 2, unless a time correction of about 4.5 hours is used, which is unjustifiable.

Other investigators, especially van Iterson (15), believe that the vulcanization reaction is autocatalytic, basing their conclusion on curves of the type of No. 2, Figure 2. However, the other two types of curves show no evidence of an autocatalytic mechanism and no indication as to when autocatalysis is to be expected.

A theory of rubber vulcanization based on the assumption that two types of rubber are formed by sulfur addition—namely, hard and soft—was put forward by Boggs and Blake

(5), who thus attempted to correlate the kinetics of vulcanization. According to this view, sulfur addition proceeds first by adding sulfur to the end double bonds of the polyprene molecule, producing soft rubber. This reaction alone is catalyzed by vulcanization accelerators and has a zero heat of reaction. Further sulfur addition takes place along the polyprene chain after the soft-rubber reaction has been completed. This they termed the hard-rubber reaction, and assumed

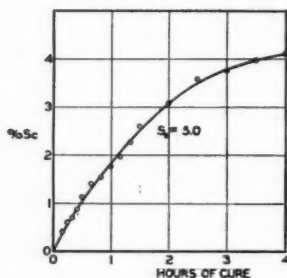


FIGURE 1. COMBINED SULFUR VS. TIME OF CURE FOR A LOW-SULFUR ACCELERATED MIX (16)

that its rate is independent of accelerators and that it liberates an appreciable heat of vulcanization.

Their conclusions were based mainly on two things: (a) the assumption that the heat of vulcanization of rubber is zero up to a coefficient of vulcanization of 3.6 to 6, whereas higher coefficients correspond to a considerable heat evolution; (b) the behavior of rubber and selenium mixes.

Their first premise was based upon a misinterpretation of their own data on the heat effect. Figure 3a is taken from Blake's article and shows the curve he drew to represent the points, falling to a value of zero at 6 per cent. However, the ordinates of this curve are calories per gram of original rubber, whereas the abscissas are grams of combined sulfur per hundred grams of mix. In other words, the two scales are not on a comparable basis. Figure 3b

shows these data plotted on a stoichiometrically comparable basis, and inspection gives no ground for representing the points other than by a straight line through the origin. Blake considered the heat evolution proportional to the amount of combined sulfur above 6 per cent. This too corresponds to a straight line on Figure 3a starting at 6 per cent and rising to the right. The dotted line is drawn by the method of least squares to pass through Blake's points. The average deviation of Blake's data points from this line is 27 per cent, whereas from the full line through the origin it is less than 6 per cent. The data of Blake demonstrate that the heat of vulcanization of rubber by sulfur is proportional to the combined sulfur from the start, rather than otherwise.

The second fact on which their theory was based is that they were never able to prepare a substance resembling hard rubber by vulcanization with either selenium or nitro compounds and that only a limited amount of either of these substances, much less than required for theoretical saturation of the double bonds, was chemically combined. It seems neither profitable nor justifiable to base a theory of the reaction of sulfur with rubber primarily on an analogy with the reaction of other chemical substances.

It is natural to assume that the reaction between sulfur and the double bonds of rubber is second order, of the type, $R + S = RS$, the rate of formation of combined sulfur being

$$\frac{dS_c}{d\theta} = K(R)(S) = K(47 - S_c)(S) \quad (1)$$

Equation 1 assumes the usual basis of 100 grams of raw rubber. S is the amount of free sulfur in grams per hundred grams of raw rubber present in the mix at the variable time, θ , during the cure. S_c is the chemically combined sulfur corresponding thereto. S_0 is the free sulfur initially

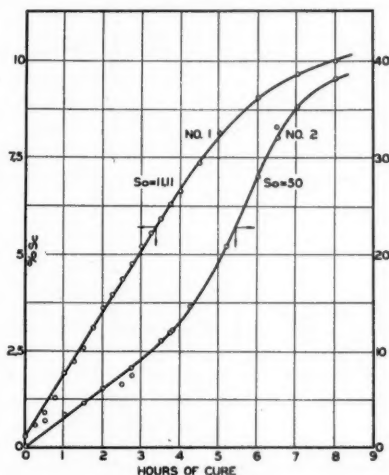


FIGURE 2. COMBINED SULFUR vs. TIME OF CURE FOR UNACCELERATED MIXES

1. $S_0 = 11.11$ (10)
2. $S_0 = 50$ (27)

present per hundred grams of rubber and, except for losses during cure, is equal to the sum of S_0 and S . Since the theoretical sulfur-combining capacity of 100 grams of rubber (C_4H_8) is 47 grams of sulfur, the equivalent amount of rubber left uncombined at any specific time during the cure is $(47 - S_0)$.

This formulation of the expression for reaction rate assumes the rate proportional to the concentrations, despite the fact that these concentrations are very high. It also assumes the effective concentration of the rubber proportional to the concentration of the double bonds, rather than to that of any specific molecular species. Although from the point

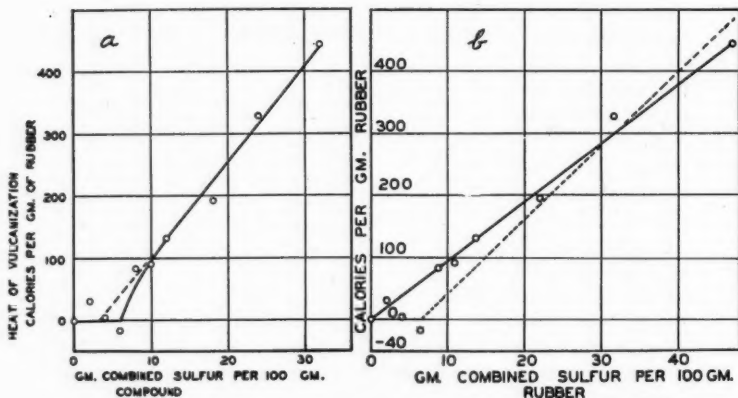


FIGURE 3. HEAT OF VULCANIZATION AS A FUNCTION OF COMBINED SULFUR (4)

- a. Incorrect basis
b. Comparable basis; dotted line drawn on assumptions that heat effect is zero up to $S_0 = 6.0$

of view of reaction kinetics these assumptions are undoubtedly open to objections, they may serve as satisfactory first approximations in which deviations from the ordinary interpretation of a reaction rate may well be absorbed in the numerical value of the constant.

Integration of Equation 1 gives:

$$\log \frac{47 - S_e}{S} = \frac{K(47 - S_0)\theta}{2.3} + \log 47/S_0 \quad (2)$$

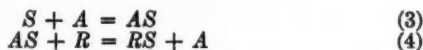
Accordingly, if the reaction is second order, the left-hand term of Equation 2 when plotted against the time of cure should give a straight line whose slope is proportional to the specific reaction constant, K , and whose intercept is proportional to the logarithm of the initial sulfur. Figure 4 shows the data of Figures 1 and 2 plotted in this way. In the early stages of cure the data follow Equation 2 fairly well, but, as the cure progresses, increasing deviations from a straight-line

relation occur. It is evident, therefore, that the assumption of a second-order reaction between rubber and sulfur does not adequately explain the kinetics of vulcanization.

It is possible to explain in a qualitative way the deviation of the reaction from a strictly second-order mechanism by assuming that a thermal depolymerization of the rubber takes place during cure which increases its reactivity. This explanation has been put forward by Axelrod (1), Hauser (14), and others. However, as will appear later, this theory is unnecessary to explain the facts. (This laboratory has recently obtained experimental evidence, to be published elsewhere, which refutes the fundamental postulate of this theory, demonstrating that thermal depolymerization during cure is not a significant factor influencing the rate of sulfur addition.)

Reaction Kinetics for Soft Rubber

The mechanism by which accelerators catalyze sulfur addition has been logically explained by Bedford and Sebrell (2) who showed that accelerator and sulfur react to form a sulfur complex which, in turn, reacts with the double bonds of the rubber to form rubber sulfide, thus regenerating the accelerator.¹ If this is true, vulcanization occurs as follows:



These reactions are consecutive. If the change in concentration of accelerator sulfide is neglected, the rate of vulcanization as measured by formation of combined sulfur will be given by the following equation:

$$\frac{dS_c}{d\theta} = k_1(A)(S) = k_2(AS)(R) \quad (5)$$

NOTE: Equation 5 is an approximation since it neglects the effect on the rate of change of accelerator sulfide concentration with time. A more exact equation may be derived as follows:

$$S_0 = S + S_c + AS \quad (6)$$

$$\frac{dS_c}{d\theta} = -\frac{dS}{d\theta} - \frac{d(AS)}{d\theta} \quad (7)$$

$$A_0 = A + AS \quad (8)$$

$$\frac{dA}{d\theta} + \frac{d(AS)}{d\theta} = 0 \quad (9)$$

$$-\frac{dS}{d\theta} = k_1(A)(S) = k_1(A_0 - AS)(S_0 - S_c - AS) \quad (10)$$

$$\frac{dS_c}{d\theta} = k_2(AS)(47 - S_c) \quad (11)$$

¹ The action of agents such as dipentamethylenethiuram tetrasulfide (Tetrone A), which are themselves sulfur complexes and produce vulcanization and cure without the use of free sulfur, substantiates the interpretation of Bedford and Sebrell. The impossibility of successfully producing vulcanized rubber without the use of some kind of catalyst makes it appear that the mechanism of Bedford and Sebrell for synthetic accelerators should also hold for the natural accelerators occurring in crude rubber.

$$\frac{d(AS)}{d\theta} = \frac{d[(dS_e/d\theta)/(47 - S_e)]}{d\theta} \frac{1}{k_2} \quad (12)$$

Substituting the values of $-dS/d\theta$ from Equation 10, AS from 11, and $d(AS)/d\theta$ from 12 into Equation 7 gives:

$$\begin{aligned} \frac{dS_e}{d\theta} = k_1 \left[A_0 - \frac{1}{k_2} \left(\frac{dS_e}{d\theta} \right) / (47 - S_e) \right] \\ \left[S_0 - S_e - \frac{1}{k_2} \left(\frac{dS_e}{d\theta} \right) / (47 - S_e) \right] - \frac{1}{k_2} \frac{d[(dS_e/d\theta)/(47 - S_e)]}{d\theta} \end{aligned} \quad (13)$$

Reaction Types

From Equation 5 we may deduce two important special cases of reaction types.

CASE 1. If reaction 3 is much faster than 4, either because k_1 is numerically much greater than k_2 , or the product of the sulfur and accelerator concentration is higher than that of the rubber and accelerator sulfide, or any combination of the two factors, study of the situation will make it clear that the accelerator will exist predominantly in the form of accelerator sulfide. Consequently, the concentration of accelerator sulfide will remain substantially constant. The equations show that the rate of rubber addition will be proportional to the concentration of uncombined rubber and completely unaffected by the variations in the concentration of free sulfur, so long as these conditions obtain. This situation may be paraphrased briefly by saying that under these conditions reaction 4 is the controlling factor in the determination of the reaction rate. Since practically all of the accelerator present in the mix will, for this case, exist in the form of accelerator sulfide, the molal concentration of AS is numerically equal to the initial concentration of accelerator in the mix, A_0 . (Clearly if the reaction of the accelerator with sulfur to form accelerator sulfide is very slow, whereas any accelerator sulfide once formed reacts extremely rapidly with rubber to regenerate the accelerator, only a small fraction of the total accelerator present will at any instant be in the form of its sulfide. This is equivalent to saying that substantially all the accelerator is at all times present in the mix in the uncombined form, and hence its concentration is for practical purposes identical with the original concentration of accelerator in the mix.) The rate of vulcanization is given by:

$$\frac{dS_e}{d\theta} = k_2 A_0 (47 - S_e) \quad (14)$$

Using the same limits of integration as in Equation 2, Equation 14 is integrated to give:

$$\log \left(\frac{1}{47 - S_e} \right) = \frac{k_2 A_0}{2.3} (\theta) + \log (1/47) \quad (15)$$

Equation 15 shows that, when reaction 4 is controlling, the logarithm of $1/(47 - S_c)$ should be linear with the time of cure, and the slope of this curve is proportional to the product of the specific reaction-rate constant and the concentration of accelerator initially present.

CASE 2. If, on the other hand, reaction 4 is the faster, then, in the sense used in the preceding case, reaction 3 controls. The same argument used in case 1 as to the form of the accelerator applies here, with the difference that the accelerator is mostly present in the uncombined state, or A . The rate in this case is given by:

$$\frac{dS_c}{d\theta} = k_1(A)(S) = k_1(A_0)(S) = k_1(A_0)(S_0 - S_c) \quad (16)$$

It is highly probable that the sulfur dissolved in the rubber exists as a molecule containing a relatively large number of sulfur atoms—i. e., as S_n , where the subscript, n , is unknown. Consequently the reaction rate equation should be written

$$\frac{dS_c}{d\theta} = k_1(A^n)(S_n) = k_1(A_0^n)(S_n)$$

However, it is readily shown that, provided n has a constant value, this expression is quantitatively equivalent to the one used in Equation 16, requiring only a differential numerical value of the coefficient of reaction rate k_1 . Because of this fact, together with the absence of data as to the value of n , the simpler equivalent expression has been used throughout.

Equation 16 may be integrated to give:

$$\log(1/S) = \frac{k_1 A_0}{2.3} \theta + \log(1/S_0) \quad (17)$$

Consider a case in which conditions are such that reaction 3 is controlling throughout the cure up to complete exhaustion of the sulfur. Equation 16 shows that the reaction rate, $dS_c/d\theta$, must in this event be proportional to the free sulfur. However, the free sulfur is at all times equal to the initial sulfur less the combined sulfur. Consequently the

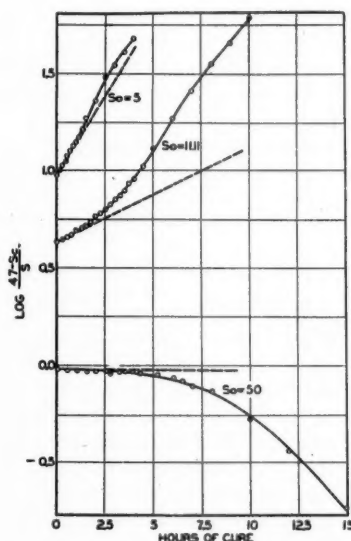


FIGURE 4. VULCANIZATION DATA PLOTTED ACCORDING TO SECOND-ORDER REACTION EQUATION

reaction rate must be linear in combined sulfur, and, as will appear, it is preferable to plot it against this variable. This has been done for this case in Figure 5a (solid line).

Now consider a case in which conditions are such that reaction 4 is controlling throughout the cure. Equation 14 shows that the rate is proportional to the concentration of rubber which, however, is proportional to $(47 - S_c)$. Here, too, the rate will be linear in combined sulfur. Consequently combined sulfur as an abscissa affords a direct basis of comparison between reaction rate in the two cases. A case of this sort is plotted in Figure 5b (solid line).

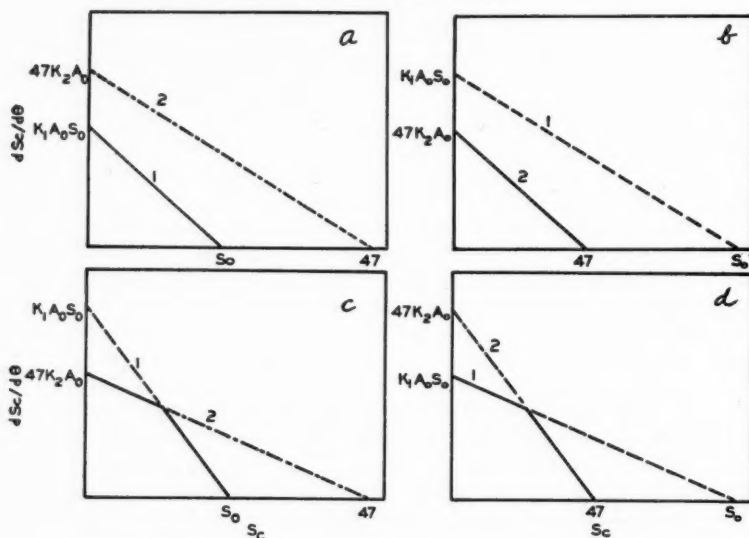


FIGURE 5. RATE OF SULFUR COMBINATION AS A FUNCTION OF COMBINED SULFUR

Solid line indicates reaction that controls.

It should be remembered that, plotted against S_0 , the rate will be linear whether one is speaking of the rate corresponding to either reaction 3 or 4 controlling. Where the rate of one reaction is far below that of the other, the actual rate will be substantially equal numerically to the lower rate. Consequently, in Figure 5a the rate will actually correspond throughout the cure to line 1, whereas in Figure 5b it will correspond to line 2.

However, there is inherently no reason why one of these lines should always lie far above the other. In special cases they may well cross each other as shown in Figures 5c and d. In these cases the character of the reaction-rate equation will change fundamentally during the process of cure.

It must always be kept in mind that, when the reaction rates corresponding to the two equations are of the same order of magnitude, as in the neighborhood of the intersec-

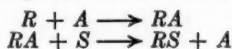
tions of the lines of Figures 5c and d, neither reaction is truly controlling, but the actual rate is determined by a balance between the two. However, the phenomena will be most clearly understood by ignoring this interference for the moment and assuming in all cases that the reaction of the lower rate is truly controlling.

The conditions determining the relative importance of reactions 3 and 4 in controlling the actual reaction rate are of interest. Equation 14 shows that the initial rate of vulcanization—i. e., when $S_e = 0$ —is proportional to the amount of free rubber present when reaction 4 controls; Equation 16 shows that the initial rate, when reaction 3 controls, is proportional to the initial sulfur. Furthermore, the particular reaction which controls is determined by the ratio k_1/k_2 and the amount of free sulfur initially present. Let the ratio k_1/k_2 be defined as α , which is, therefore, a quantity depending only upon the particular type of accelerator under consideration and the temperature. There are several reaction types which are now theoretically possible.

Possible Reaction Types

TYPE A. If the initial free sulfur is less than $47/\alpha$ and 47, reaction 3 controls throughout the entire cure. This may be shown graphically as in Figure 5a where the rate of disappearance of free sulfur is plotted as a function of combined sulfur. It is easy to show that, if S_0 is less than $47/\alpha$, then $47 k_2 A_0$ is greater than $k_1 A_0 S_0$; and since S_0 is less than 47, the rate of reaction 3 is always less than reaction 4 and hence reaction 3 controls all the way.

The mechanism of accelerator action here postulated—namely, the formation of an intermediate accelerator-sulfur complex—seems to be well established on chemical grounds. It should be pointed out, however, that as far as the kinetics of sulfur addition are concerned, other assumptions as to the type of reaction mechanism will give rise to rate equations similar to those here derived. Thus, assuming that the accelerator adds first to the rubber forming an accelerator-rubber complex, the reactions would be



Carrying through the same analysis as above shows that, when S_0 is less than $47/\alpha$ and less than 47, the reaction rate is proportional throughout the cure to the free sulfur, etc. However, in view of the fact that accelerator-sulfur complex will produce sulfur addition and vulcanization and in view of the lack of knowledge of the existence and effectiveness of other types of accelerator complexes, reactions 3 and 4 will be assumed to take place.

TYPE B. If the initial free sulfur is greater than $47/\alpha$ and less than 47, reaction 4 will control at the start, and the initial rate of vulcanization will be independent of the initial free

sulfur. Reaction 3 will control later in the cure. This is shown graphically in Figure 5c where the rate of reaction 3 is greater at first because $k_1 A_0 S_0$ is much larger than $47 k_2 A_0$. Later in the cure, however, the rate of reaction 4 becomes greater so that reaction 3 controls.

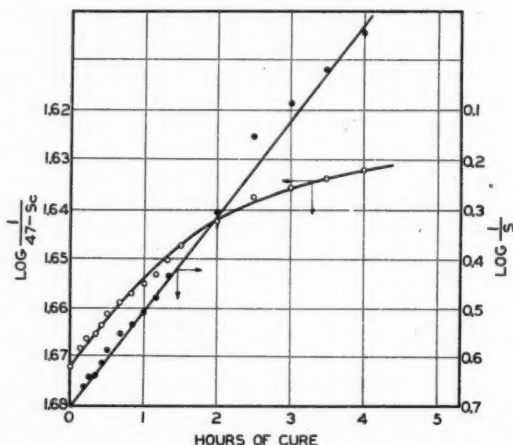


FIGURE 6. DATA OF KRATZ AND FLOWER (16) PLOTTED ACCORDING TO EQUATIONS 15 AND 17

TYPE C. If the initial free sulfur is greater than $47/\alpha$ and 47, reaction 4 should control all the way, and we obtain the type shown in Figure 5b. This case should apply to hard rubber, but, as will be seen later, the experimental facts are more complicated than would appear from the analysis of this type.

TYPE D. Another reaction type is theoretically possible from Equations 14 and 16. If the initial free sulfur is less than $47/\alpha$ but greater than 47, reaction 3 should control at the start, followed by reaction 4. This case, apparently, has never been realized experimentally for sulfur mixes. (Figure 5d).

Analysis of Experimental Data

The above analysis was made on the assumption that an acceleration is a necessary adjunct to vulcanization. The experimental data available will now be examined to see how well they check the theory.

Figure 6 shows the data of Kratz and Flower taken from Figure 1 and plotted according to Equations 15 and 17. The plot of Equation 15 is a smooth curve; that of Equation 17 is a straight line within the experimental error. We may conclude, therefore, that this is a type A reaction in which the rate is controlled by the rapidity with which sulfur combines with the accelerator.

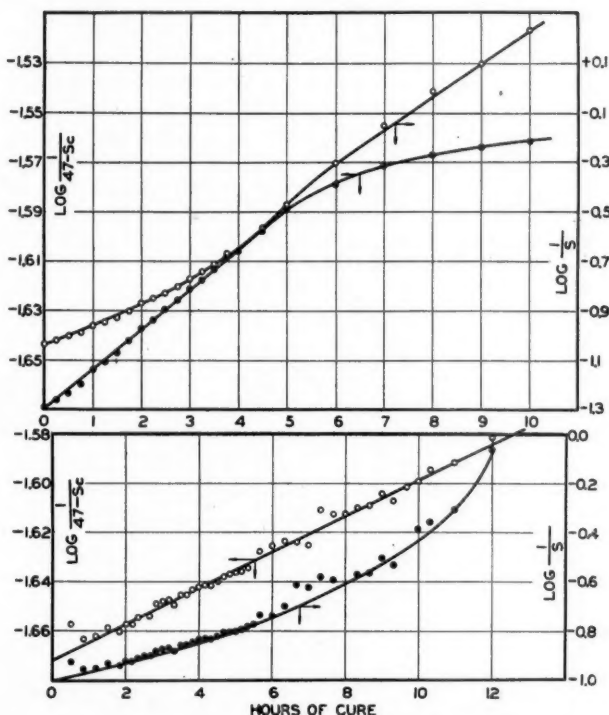


FIGURE 7 (Above). DATA OF EATON AND DAY (10) PLOTTED ACCORDING TO EQUATIONS 15 AND 17

FIGURE 8 (Below). DATA OF GOTTLOB (13) PLOTTED ACCORDING TO EQUATIONS 15 AND 17

Figure 7 shows the data of Eaton and Day from curve 1, Figure 2, plotted according to Equations 15 and 17. This shows clearly the behavior predicted for a type B reaction. The plot of the logarithm of $1/(47 - S_c)$ is linear with the time of cure up to about 4.5 hours.¹ From there on the values

¹ An apparent contradiction exists here since curve 1, Figure 2, shows that for these data S_c is also linear with time of cure. The explanation lies in the fact that the data follow Equation 15, which may also be expressed as

$$S_c = 47[1 - e^{-(k_2 A_0 \theta)}]$$

or expanding the left-hand side as a power series, as follows:

$$S_c = 47 \left[k_2 A_0 \theta - \frac{(k_2 A_0 \theta)^2}{2!} + \frac{(k_2 A_0 \theta)^3}{3!} \dots \right]$$

Thus for sufficiently small values of θ , S_c is proportional to $47 k_2 A_0$ and for large values of θ , the departure of S_c from linearity depends upon the magnitude of $k_2 A_0$. Neglecting the terms in the expansion beyond the first and taking $k_2 A_0$ to be 0.0377 for the data of Eaton and Day, it can be shown that the value of S_c is only a few per cent higher than calculated by the exponential expression, at $\theta = 3$. Therefore, because of lack of precision in the data, both the linear and the exponential expressions will fit the data in this range.

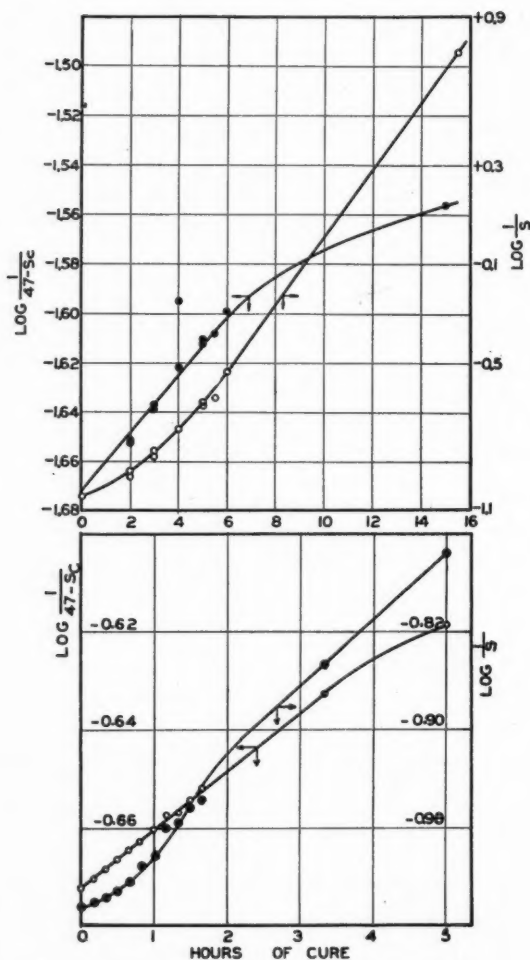


FIGURE 9 (Above). DATA OF BLAKE (3) PLOTTED ACCORDING TO EQUATIONS 15 AND 17

FIGURE 10 (Below). DATA OF NAGEL (21) PLOTTED ACCORDING TO EQUATIONS 15 AND 17

deviate from the straight line and fall upon a smooth curve. On the other hand, if we plot the logarithm of $1/S$ against time, the values fall on a smooth curve which bends upward, as far as 4.5 hours. Beyond that time the points lie nearly on a straight line, as would be predicted by the theory.

The two reaction constants may be calculated for this cure since both reactions play a part. From the slope of the straight lines in Figure 7 we may calculate $k_1 A_0$ to be 0.309,

k_2A_0 to be 0.03765, and $47/\alpha$ to be 5.74. This value is considerably less than the initial free sulfur of 11.11, as it should be according to the theory.

A large number of the vulcanization studies reported in the literature are apparently of type B; for instance, Figure 8 shows the data of Gottlob (13). The details of this cure are given in Table I. In spite of the fact that this cure was continued for 12 hours the ratios of k_1A_0 to k_2A_0 were such that a point was never reached in which reaction 3 controlled. Table I and Figures 9 and 10 show data taken in the laboratory on pure gum mixes.

TABLE I. DETAILS OF CURES

Reaction Type	Temp. °C.	S_0	k_1A_0	k_2A_0	Remarks	Reference
A	144.5	6	4.0	1 ZnO; 0.5 diethyl-ammonium diethyldithiocarbamate	(9)
A	148	5	0.446	100 ZnO; 0.33 basic amine	(16)
A	140	3.01	1.904	5 ZnO; 1 diphenylguanidine	(32)
A	138	5.0	1.127	1 Vulcasit	(25)
A	138	3.09	0.1645	(26)
A	138	5.28	0.1645	(26)
B	140	11.11	0.327	0.0265	(3)
B	140	7.68	1.025	0.1215	5 ZnO; 1 diphenylguanidine	(7)
B	144.5	6	0.94	0.0247	1 ZnO	(9)
B	144.5	6	"	0.0801	1 ZnO, 1/2 hexamethylene tetramine	(9)
B	140	11.11	0.709	0.0799	Smoked sheets	(10)
B	140	11.11	0.309	0.03765	Slab rubber	(10)
B	140	11.11	0.426	0.029	Pale crepe	(10)
B	147.1	8.11	0.764	0.060	(11)
B	142	11.11	0.327	0.0265	(3)
B	141.5	8.1	"	0.0199	(17)
B	141.5	8.1	"	0.0359	0.93 aniline	(17)
B	141.5	8.1	"	0.0197	100 ZnO	(17)
B	141.5	8.1	"	0.0314	100 ZnO; 0.93 aniline	(17)
B	141.5	8.1	"	0.0275	2.28 diphenylthiourea	(17)
B	141.5	8.1	"	0.0408	2.28 diphenylthiourea; 100 ZnO	(17)
B	138	10	"	0.01683	(13)
B	140	11.11	0.128	0.02715	(21)
B	140	14.44	"	0.1535	5 ZnO; 1 diphenylguanidine	(32)
B	138	10	1.127	0.116	1% Vulcasit	(25)
B	138	10	"	0.01615	(25)
B	138	15	1.127	0.195	1% Vulcasit	(25)
B	135	9.41	"	0.01175	Acetone-extd. pale crepe	(28)
..	...	11.11	"	(28)
B	135	8.2	0.401	0.090	(28)
..	...	11.11	"	(28)
B	138	11.11	"	0.026	(30)
B	138	11.11	"	0.0484	1/2 aldehyde ammonia	(30)
B	138	11.11	"	0.075	1/2 aldehyde ammonia	(30)
B	138	11.11	"	0.1485	1/2 aldehyde ammonia	(30)
B	138	11.11	"	0.212	1 aldehyde ammonia	(30)
B	118	11.11	0.0843	0.01595	1/2 aldehyde ammonia	(30)
B	118	11.11	0.1457	0.0269	1/2 aldehyde ammonia	(30)
B	118	11.11	0.0488	0.299	1 aldehyde ammonia	(30)
B	140	20	"	0.0332	(23)
C	140	50	"	0.0705	(27)

* Because the cure was not continued sufficiently long, it was impossible to calculate the values of k_1A_0 in all cases.

For types A and B it is possible to predict the effect of varying the amount of initial free sulfur in a mix when holding the other conditions, such as temperature, amount of accelerators, fillers, etc., constant. For a set of uniform mixes in which the amount of initial sulfur is gradually increased, the reaction should change from type A to type B as the initial free sulfur becomes greater than $47/\alpha$. A comparison of this sort is shown in Figure 11 on data from this laboratory (Table I, references 7 and 32). This mix consisted of 100 parts rubber, 1 diphenylguanidine, 5 zinc oxide, and varying amounts of initial free sulfur; the temperature of the cure was 140°C . At low S_0 —namely, 3.01—the reaction is type A, with Equation 17 plotted as a straight line (Figure 11b). When the initial free sulfur is high (14.44 per cent), the reaction is clearly type B; that is, Equation 15 holds throughout the range of data, not reaching a transition point (Figure 11a), whereas Equation 17 gives a curve that is concave upward. The only factor varied in these two mixes was the amount of initial free sulfur. One should be able to calculate k_1A_0 from the low-sulfur curve and k_2A_0 from the high-sulfur curve and compare them at intermediate values of initial free sulfur. From the slope of the straight lines k_1A_0 is 1.90 and k_2A_0 is 0.154. Then $47/\alpha$ is 3.8, and the reaction type should change from A to B at an initial sulfur content of about this value. Confirming this assumption, a cure containing an initial free sulfur of 7.68 is of type B. Furthermore, Figure 12, where the rate of reaction is plotted against combined sulfur, shows that for an initial sulfur content of 7.68, the point at which reaction 4 ceases to control and reaction 3 begins is approximately at a combined sulfur value of 4.2 per cent. By substituting the value of S_0 and that for k_2A_0 found above, in Equation 15, the time of cure at which the reaction type should change was calculated to be 0.6 hour. Referring to the curves of Figure 11 for this mix, the actual break approximates this value closely, occurring at about 0.5 hour.

So far only those mixes in which the amount of accelerator was kept constant have been considered. When the amount of accelerator is varied from cure to cure, keeping other conditions constant, a much more complicated behavior results. Unfortunately few data are available to test this point thoroughly. The most complete seems to be that of Twiss and Brazier (30). These authors determined the coefficient of various kinds of cures for mixes made up of 100 parts rubber, 11.11 sulfur, and varying amounts of accelerator; the temperature was varied to obtain the temperature coefficient of the reaction. However, the data of Twiss and Brazier are presented as graphs, and no actual data are given. In order to determine the reaction rate, it is necessary to read the combined sulfur values from a small plot, and large errors are certain to occur. Table II gives the coefficients of vulcanization scaled off the plot of Twiss and Brazier

as accurately as possible, for the various temperatures. Figure 13 shows the results obtained when Equations 15 and 17 are plotted for the 148° and 128° C. cures. From the slopes of these lines the values of reaction constants k_1A_0 and k_2A_0 were determined. Figure 14 shows the values of the reaction constants read from Figure 13 and plotted against the per cent accelerator added. These points fall on straight lines within the precision of reading the data of the plot.

Figure 14 shows, as might have been expected, that the added accelerator behaves independently of the natural accelerator of the crude rubber and that the effects of the two are additive. This is a case of simultaneous or concurrent reactions.

This type may be formulated analytically as follows: Each accelerator present, in this case the natural and the added accelerator, may be assumed to react with sulfur and rubber according to Equation 5, and each acts independently of the other. The rate of formation of combined sulfur will then be the sum of the rates by which it is produced due to each of the accelerators present. This fact is expressed in Equation 18 where subscripts n and a refer to the rates of vulcanization of the natural and added accelerators, respectively:

$$\begin{aligned}\frac{dS_c}{d\theta} &= \left(\frac{dS_c}{d\theta}\right)_n + \left(\frac{dS_c}{d\theta}\right)_a \\ &= (k_1A_0)_n(S) + (k_1A_0)_a(S) = (k_2A_0)_n(47 - S_c) + (k_2A_0)_a(47 - S_c) \\ &= [(k_1A_0)_n + (k_1A_0)_a] S = k_1A_0S \\ &= [(k_2A_0)_n + (k_2A_0)_a] (47 - S_c) = k_2A_0(47 - S_c) \quad (18)\end{aligned}$$

Equation 18 shows that the product of the reaction constant and the initial concentration of accelerator can be written as the sum of similar products for each accelerator; expressed another way, the over-all specific reaction constant is a linear function of the concentration of added accelerator. This fact is expressed in Equation 19:

$$kA_0 = (kA_0)_n + (kA_0)_a = a + b (\% \text{ added accelerator}) \quad (19)$$

Figure 14 shows that the slopes of the straight lines are equal numerically to the specific reaction constant, $(k)_a$, of the added accelerator for the particular reaction 3 or 4 in question. The intercept of the ordinate for 0 per cent accelerator represents kA_1 of the natural accelerator of the rubber.

Table III represents the reaction constants calculated from data of Twiss and Brazier at several temperatures for the natural and added accelerator. In this case the added accelerator was aldehyde ammonia. The data of Twiss and Brazier are insufficient to draw definite conclusions as to the trend of these reaction constants with temperature. However, a

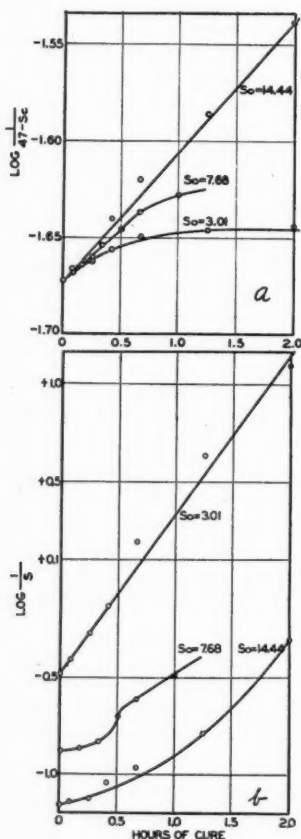


FIGURE 11. DATA OF CAPPELLO (7) AND WILDER (32) ON EFFECT OF VARIATION OF INITIAL SULFUR

a. Plotted according to Equation 15
b. Plotted according to Equation 17

comparison of the last two columns of Table III tend to indicate that, as the temperature of the cure is raised, the efficiency of the natural accelerator as measured by the ratio α tends to increase while that of the added accelerator tends to decrease, although the absolute values of the constants are increasing with the temperature during this period. This is in conformity with the observations of Glancy, Wright, and Oon (12) who found that accelerators which were active in soft rubber compounds were relatively poor when used for curing hard rubber at high temperatures. It seems highly important for an adequate understanding of vulcanization and accelerator action that kinetic data more accurate and dependable than those of Twiss and Brazier be obtained; work of this nature is now in progress in this laboratory.

Hard Rubber

The intermediate accelerator sulfide theory has been shown to explain

adequately the kinetics of low-sulfur cures, both for accelerated and nonaccelerated mixes. However, it is obvious that the equations developed cannot apply to a cure in which the rate of vulcanization shows an increase during the cure. Curve 2, Figure 2, shows that the rate of vulcanization is practically constant up to about 4.5 hours, but from 4.5 to 7 hours it increases rapidly. This behavior is usually exhibited by high-sulfur mixes—i. e., those in which the initial sulfur is greater than 20—and is one of the most puzzling features of the kinetics of sulfur addition.

This increase in rate for hard-rubber vulcanization must be analyzed on the basis of two well-substantiated facts. In the first place, rubber is extremely low in thermal conductivity

TABLE II. DATA OF TWISS AND BRAZIER WHEN $S_0 = 11.11$

Temp. ° C.	Accelerator %	Time Min.	S	$47 - S_0$	$-\text{Log } 1/S$	$-\text{Log } \frac{1}{47 - S_0}$
148	1.00	10	7.11	43.0	0.852	1.6335
		12	6.01	41.9	0.779	1.6221
		14	5.51	41.4	0.741	1.6170
		18	4.50	40.4	0.654	1.6068
		20	4.01	39.9	0.603	1.6010
	0.5	15	7.51	43.4	0.876	1.6374
		20	6.61	42.5	0.821	1.6285
		25	5.11	41.0	0.708	1.6127
	0.25	20	7.91	43.8	0.898	1.6415
		25	6.81	42.7	0.833	1.6305
		30	6.11	42.0	0.786	1.6233
		40	4.61	40.5	0.688	1.6075
	0.125	30	8.11	44.0	0.909	1.6435
		45	6.81	42.7	0.833	1.6305
		50	6.21	42.1	0.793	1.6242
		60	5.41	41.3	0.733	1.616
	0	50	8.31	44.2	0.9195	1.6455
		60	7.91	43.8	0.898	1.6415
		80	6.31	42.2	0.800	1.6253
		85	6.11	42.0	0.786	1.6232
		90	5.61	41.5	0.749	1.618
138	1	15	8.81	44.7	0.945	1.6504
		20	8.31	44.2	0.9195	1.6454
		30	6.81	42.7	0.833	1.6315
		35	5.81	41.7	0.764	1.6203
		40	4.91	40.8	0.691	1.6107
	0.5	20	8.81	44.7	0.945	1.6505
		30	7.91	43.8	0.877	1.6415
		35	7.11	43.0	0.854	1.6335
		45	6.01	41.9	0.779	1.6223
		55	5.11	41.0	0.7085	1.6128
	0.25	30	9.71	45.6	0.987	1.659
		50	8.61	44.5	0.935	1.6483
		60	7.71	43.6	0.887	1.6395
		70	6.91	42.8	0.8395	1.6313
		80	6.11	42.0	0.786	1.6234
		90	5.41	41.3	0.733	1.616
	0.125	90	7.71	43.6	0.877	1.6395
		120	6.81	42.7	0.833	1.6305
		140	6.11	42.0	0.786	1.623
		160	5.41	41.3	0.733	1.616
	0	150	8.31	44.2	0.9195	1.6455
		180	7.61	43.5	0.833	1.6385
		200	7.21	43.1	0.858	1.6345
		230	6.21	42.1	0.793	1.6242
		260	5.71	41.6	0.757	1.619
128	1.00	30	9.11	45.0	0.9595	1.6532
		45	7.41	43.4	0.8691	1.6375
		60	6.91	42.9	0.8395	1.6325
		70	6.11	42.1	0.7860	1.6243
		80	5.11	41.0	0.7084	1.6128
		90	4.61	40.6	0.6637	1.6085
	0.5	60	9.31	44.2	0.9689	1.6454
		80	7.51	43.4	0.8756	1.6375
		100	6.71	42.6	0.8267	1.6294
		110	5.91	41.8	0.7716	1.6212
	0.25	120	7.71	43.6	0.8871	1.6395
		140	7.11	43.1	0.8519	1.6345
		170	6.51	42.4	0.8136	1.6274
		190	6.11	42.0	0.7860	1.6232
		220	5.11	41.0	0.7084	1.6128
	0.125	270	6.61	42.5	0.8202	1.6284
		300	6.01	41.9	0.7789	1.6222
		320	5.71	41.6	0.7566	1.6191
		360	4.91	40.8	0.6911	1.6107
	0	450	6.81	42.7	0.8331	1.6304
		500	6.31	42.2	0.8000	1.6253
		540	5.71	41.6	0.7566	1.6191
		580	5.21	41.1	0.7168	1.6138

TABLE II (continued)

Temp. ° C.	Accelerator %	Time Min.	S	47 - S _c	-Log 1/S	-Log $\frac{1}{47 - S_c}$
118	1.0	120	7.11	43.0	0.8591	1.6335
		140	6.61	42.5	0.8202	1.6284
		160	6.11	42.0	0.7860	1.6232
		180	6.01	41.9	0.7789	1.6222
		200	5.41	41.3	0.7332	1.6160
	0.5	180	7.71	43.6	0.8871	1.6395
		210	7.21	43.1	0.8579	1.6345
		240	6.31	42.2	0.8000	1.6253
	0.25	260	6.01	41.9	0.7789	1.6222
		300	7.61	43.5	0.8814	1.6385
		340	7.21	43.1	0.8579	1.6335
		370	6.71	42.6	0.8367	1.6294
		420	6.41	42.3	0.8069	1.6263
		460	5.81	41.7	0.7642	1.6201

and vulcanization does not change the conductivity appreciably (19). Then, it has been known for years that the chemical addition of sulfur to rubber is an exothermic reaction. Thus, Perks (24), Williams and Beaver (33), and others showed that the temperature of the interior of a rubber mix during vulcanization may rise considerably above that at the surface. Furthermore, the data of Blake (4) show that the heat evolved on vulcanization is substantially proportional to the combined sulfur.

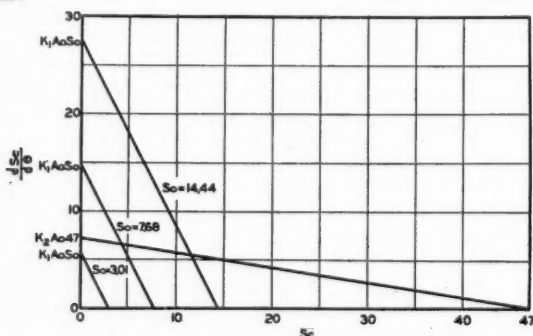


FIGURE 12. RATE OF REACTION vs. COMBINED SULFUR FROM DATA OF CAPPELLO (7) AND WILDER (32)

During vulcanization, when the sample comes up to curing temperature, sulfur addition starts with an appreciable rate. This sulfur addition generates heat. Because of the low thermal conductivity of the rubber, the rate at which this heat can escape is extremely low, and therefore part of it remains in the rubber and raises its temperature. If the sample is thin enough and the sulfur adds slowly or is small in total amount, the heat evolved will be small and will flow from the sample without raising its temperature appreciably. However, for high-sulfur cures, the temperature in the center of the sample becomes much higher than that of the surface; this in turn speeds up the reaction which liberates more heat and further raises the temperature of the sample, with the result that sulfur addi-

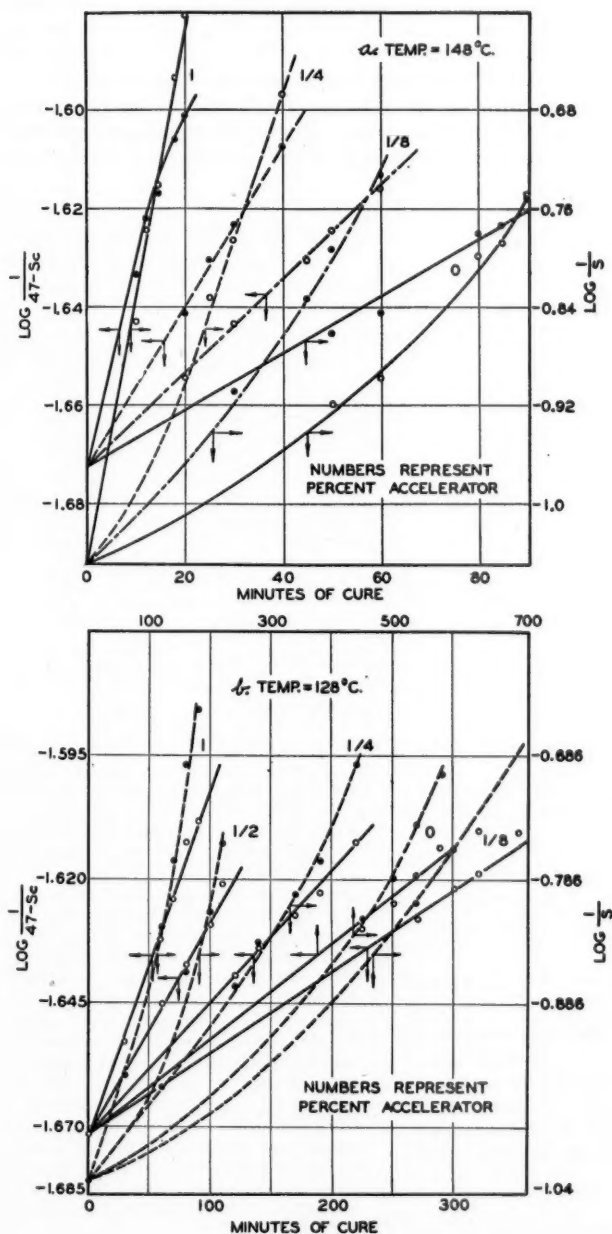


FIGURE 13. DATA OF TWISS AND BRAZIER (30) PLOTTED ACCORDING TO EQUATIONS 15 AND 17

tion is markedly accelerated and gives, in a sense, an autocatalytic effect. The data of Williams and Beaver on an accelerated low-sulfur mix cured at 175° C. are plotted in Figure 15 and show the striking temperature increase observed.

It was felt that the simultaneous determination of the temperature distribution in the sample and the combined sulfur during vulcanization would afford a conclusive test of this point:

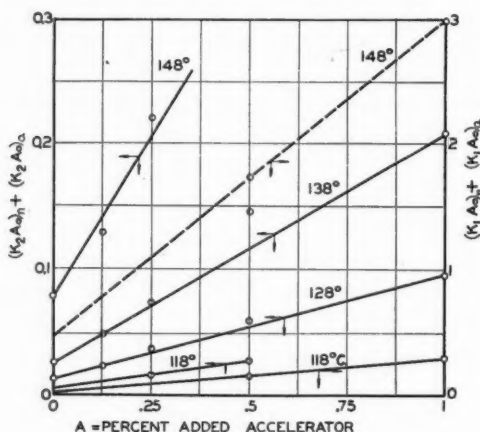


FIGURE 14. REACTION CONSTANTS *vs.* ADDED ACCELERATOR FROM DATA OF TWISS AND BRAZIER (30)

These experiments were performed on a mix composed of 100 parts rubber, 5 zinc oxide, 1 diphenylguanidine, and 50 sulfur (34). The samples were cured in individual molds made from 0.25-inch (6.35-mm.) steel plate drilled with a 1.5-inch (3.8-cm.)

hole; the mix was held in the mold by thin sheets of aluminum on either side. Curing took place in a standard, steam-heated platen press. At the start of the cure fourteen samples, each in its separate mold, were placed in the press. In the center of the mix in one of these samples a carefully calibrated thermocouple was placed; another thermocouple was placed outside of the mold, between the outer aluminum sheet and the platen, to measure the temperature at the surface of the sample. A record of both the surface and center temperatures was kept during the cure. Samples were removed from time to time, quenched in cold water, and analyzed for combined sulfur. Runs

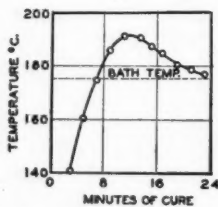


FIGURE 15. INTERNAL TEMPERATURE OF A HIGH-SULFUR MIX DURING CURE (33)

were made at 150° and 160° C. (Figure 16).

Figure 16 shows that in both cases a pronounced increase in temperature at the center of the sample was observed during cure, amounting to more than 80° for the sample

cured at 160° C. Furthermore, the rapid increase in the rate of vulcanization, as measured by the combined sulfur, always occurs in the neighborhood of the maximum temperature. In general, the maximum rate of sulfur addition occurs later than the maximum temperature recorded at the center, as might be expected, since maximum center temperature is not synchronous with maximum average temperature. Furthermore, the increase in the rate of vulcanization is more abrupt and larger for the sample cured at the higher temperature, corresponding to the more pronounced temperature maximum observed in this case.

A clearer picture of what happens can be obtained by laminating the samples into thin sheets, so that the rate of vulcanization can be followed as a function of the location in the sample as well as the time of cure:

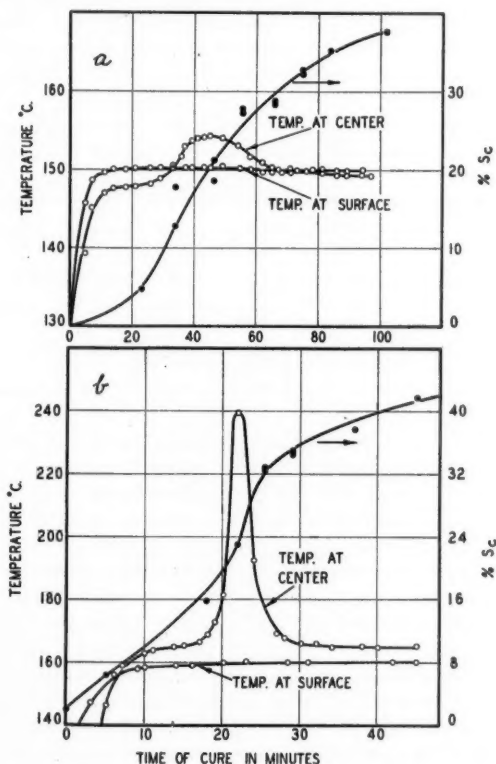


FIGURE 16. TEMPERATURE HISTORY AND COMBINED SULFUR vs. TIME OF CURE

a. 150° C. b. 160° C.

To effect this, the uncured mix was sheeted out on the mill to 0.03 inch (0.762 mm.) and cut into disks 1.5 inches (3.8 cm.) in diameter. On each of these thin sheets was centered a disk of aluminum foil 0.001 inch (0.0254 mm.) thick, of such a diameter

that at no point did it come within 0.25 inch (6.35 mm.) of the edge of the sample. These were placed in sandwich fashion in the circular molds used in the previous run, so that there were seven layers of rubber separated by sheets of aluminum foil. In one of the samples the thermocouple was placed in the center sheet and a surface thermocouple was attached as in the previous run. The samples were cured in the press, and from time to time one was removed and quenched in water and then carefully sawed and split so that four layers, each approximately 0.03 inch thick, could be obtained—namely, the surface layer, the two intermediate layers, and the center layer. Each layer was analyzed for combined sulfur separately by the usual technic. The temperature of this laminated run was 155° C.

Figures 17 and 18 give the temperature history of the center and surface of the samples and the combined sulfur of the four layers separately as a function of time of cure. Figure 18 shows that, at equal values of combined sulfur, the rate of sulfur combination as measured by the slope of the curve is always less for the surface than for the center layer. This increased rate must be due solely to the excess temperature of the center layer, since the composition of the two layers at this point in the vulcanization process is identical. Thus, under these conditions the increased vulcanization

TABLE III. REACTION CONSTANTS FROM DATA OF TABLE II

Temp., ° C.	k_1A_0	k_2A_0	$(k_1)a$	$(k_2)a$	$(k_1A_0/k_2A_0)_n$	$(k_1/k_2)a$
148	0.465	0.0795	2.57	0.520	5.85	4.93
138	...	0.026	...	0.186
128	...	0.0133	...	0.0835
118	0.0076	0.005	0.3066	0.0438	1.5	7.23

rate in the center of the sheet cannot be due to differences in such factors as sulfur solubility, since the increase in reaction rate is much less for the surface layers than for the center layers. Furthermore, the increase in the specific reaction rate at the center is, within the precision of the data, exactly the sort of temperature function that one would expect.

These data support the contention of other investigators that there is marked temperature rise in the center of a hard-rubber sample during cure. They demonstrate further that this rise is accompanied by an increased rate of sulfur addition which corresponds to the temperature change within the precision of the data. There is no evidence to indicate other significant factors as causes of the abnormalities of rate of sulfur addition in hard-rubber vulcanization. In other words, this abnormality is evidently due, in part at least, to the exothermic character of the reaction combined with the low thermal conductivity of rubber.

The vulcanization of rubber is an exceedingly complex phenomena and many important factors have been purposely

neglected in the present discussion. Thus, the specific effect of accelerators on the physical properties of the resulting product, the complicated behavior of the temperature coefficient of the reaction, etc., must be explained before our knowledge of the phenomena can be said to approach com-

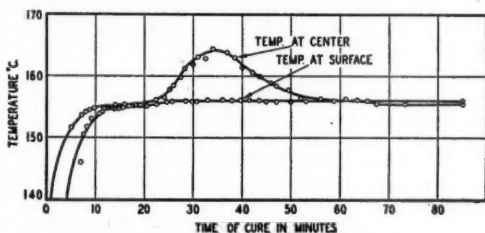


FIGURE 17. TEMPERATURE HISTORY AT CENTER OF LAMINATED SAMPLE AT 155° C.

pleteness. However, the data on the kinetics of vulcanization can be correlated by assuming (a) the existence of an intermediate accelerator-sulfur complex, which has been shown to exist by other evidence, and (b) a large temperature rise during vulcanization of hard rubber. The influence of the amount and activity of the accelerator and the concentration of rubber and sulfur on the reaction rate are capable of quantitative expression which permits the evaluation of accelerators as chemical catalysts in a straightforward and conventional manner—namely, by their influence on the specific reaction rate.

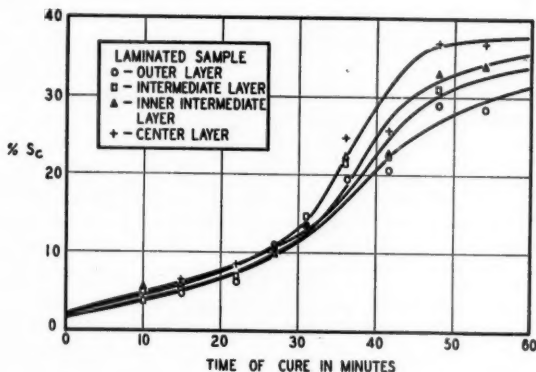


FIGURE 18. COMBINED SULFUR vs. TIME OF CURE FOR VARIOUS LAYERS OF LAMINATED SAMPLE AT 155° C.

Nomenclature

- S_0 = initial free sulfur, grams/100 grams of original raw rubber
 S = free sulfur, grams/100 grams of original rubber
 S_c = combined sulfur, equivalent to rubber sulfide (RS), grams/100 grams of original rubber

- θ = time of cure, usually hours
 R = free rubber, equivalent to $(47 - S_e)$
 RS = polyprene sulfide of vulcanized rubber
 A_0 = total accelerator concentration
 A = free accelerator concentration
 AS = accelerator-sulfur complex
 k = specific reaction constant
 K = specific reaction constant, second-order reaction
 Subscripts 1 and 2 refer to reactions 3 and 4, respectively, as indicated in Equation 5.

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The Vulcanization of Rubber with *m*-Dinitrobenzene

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The literature referring to the vulcanization of rubber with *m*-dinitrobenzene indicates the present undeveloped state of knowledge of the reaction and of the most favorable conditions for its employment. Much is vague and even contradictory.

Ostromislensky (*J. Russ. Phys.-Chem. Soc.*, **47**, 1462 (1915)) stated that certain nitro compounds are capable of vulcanizing rubber in the absence of auxiliary substances, and that the products of vulcanization are superior in some respects to sulfur vulcanizates; tensile strengths obtained were comparable with those of sulfur vulcanizates; aging properties were found to be good; color and finish were better than those of sulfur vulcanizates. On the other hand, Porritt (*J. Soc. Chem. Ind.*, **35**, 986 (1916)), and Stevens (*J. Soc. Chem. Ind.*, **36**, 107 (1917)) failed to confirm these statements, but agreed that the presence of litharge is beneficial. Again in 1929, Ostromislensky (*India Rubber World*, **80**, 55 (1929)) confirmed his original report, stating that he believed that this form of vulcanization is due to an action between rubber and the oxygen of the nitro compound.

Blake (*Ind. Eng. Chem.*, **22**, 7 (1930)) stated that vulcanization of rubber with dinitrobenzene involves a monomolecular chemical reaction between rubber and dinitrobenzene, in which, of the 6 per cent dinitrobenzene, practically all of the nitrogen combined with the rubber. The end-product of the reaction appears to be a soft vulcanized rubber; no one has claimed to be able to produce an ebonite by the use of this reagent.

Some workers, including Bunschöten (*Chem. Weekblad*, **15**, 257 (1918)) have reported considerable variations in physical properties of vulcanizates made from different types of raw rubber, each being vulcanized to the optimum cure.

In view of the conflicting opinions, it was decided to examine the physical properties of rubbers vulcanized with dinitrobenzene in the presence of various auxiliary substances with the object of finding the most stable vulcanizate with the best tensile strength. It was also hoped that some light might be thrown upon the problem of the mechanism of the vulcanization reaction.

Preliminary Experiments.—A simple mixture of crepe rubber and dinitrobenzene was first prepared. During the mixing process on open rolls it was observed that if the rolls were cold the crystals of dinitrobenzene yielded a coarse dispersion; if the rolls were moderately hot, fumes were liberated and mixing was facilitated by solution of dinitrobenzene in rubber; if the rolls were very hot the dinitrobenzene (m. p. 91° C.) melted, and the liquid dissolved in the rubber with a plasticizing action and evolution of fumes.

It is evident therefore that the conditions of mixing may possibly modify the properties of the stock, both from the point of view of its tendency to bloom and its plasticity, as recrystallization may occur on cooling. Further, visual evidence showed that loss of a part of the vulcanizing agent occurred by thermal decomposition; a fact relevant to the composition of the final product.

A simple mixture of 100 parts of rubber and 6 parts of dinitrobenzene when heated in the press for two hours at 140° C. showed none of the changes usually associated with vulcanization. A mixture of 100 parts of smoked sheet rubber, 10 parts of litharge, and 6 parts of dinitrobenzene was found to vulcanize satisfactorily in 30 minutes at 140° C. Its vulcanizing characteristics, as shown by tensile properties, were therefore compared with those of a mix consisting of 100 parts of smoked sheet rubber, 10 parts of litharge, and 6 of sulfur. The results are given in Table I.

TABLE I

Time of Cure (Min. at 141° C.)	Tensile Strength (Lbs. per Sq. In.)		Modulus at 600% Elongation (Lbs. per Sq. In.)	
	Sulfur	Dinitrobenzene	Sulfur	Dinitrobenzene
10	1800	178	280	144
17	1748	1222	420	281
24	1900	1606	475	405
31	2116	1900	520	460
38	1835	1890	530	518
45	1919	1850	570	630

The results shown in Table I indicate that the optimum cure (based on the best tensile strength) occurs in both cases after 31 minutes. The best tensile strength of the sulfur mix is only slightly greater than that of the dinitrobenzene vulcanizate. The course of the physical change differs; initial "set up" occurs later in the case of the dinitrobenzene mix.

To determine the effect of some compounding ingredients other than litharge, China clay, zinc oxide, whiting, carbon black, magnesium carbonate, barium sulfate, lithopone and a few organic accelerators were separately added to mixings of 100 parts of rubber, and 6 parts of dinitrobenzene. After heating for one and one-half hours at temperatures within the usual range, no signs of vulcanization were observed in any case.

The Effect of a Large Concentration of Dinitrobenzene.—A mixture of 100 parts of rubber, 10 parts of litharge, and 50 parts of dinitrobenzene was made. On curing for three hours at 150° C. a soft rubber vulcanizate was obtained; this had a bad surface, was porous, black in color, produced a greenish bloom, and was obviously very weak. Indeed, it showed the usual signs of overcure and no signs of the formation of a rigid product.

The Influence of Various Lead Compounds.—To each portion of a base mix consisting of 100 parts of rubber and 6 parts of dinitrobenzene, 10 parts of a lead compound were added; all samples were then heated in the press under the conditions stated below.

TABLE II

Compound of Lead	Time of Heating (Min.)	Temp. of Press (° C.)	Tensile Strength (Lbs. per Sq. In.)	Comments
Litharge (PbO)	30	141	1900*	Good cure
Red lead (Pb ₂ O ₃)	60	141	1835*	Good cure
Peroxide (PbO ₂)	60	141	1300*	Definite cure
Carbonate	60	141	Very slight cure
Chromate	80	147	Very slight cure
Nitrate	60	141	No cure
Sulfate	50	147	Very slight cure
Acetate	60	141	950*	Definite cure
Tartrate	60	141	Very slight cure
Chloride	80	147	No cure; very sticky

* Optimum cures at 141° C.

The results (Table II) show that the oxides were by far the most effective lead compounds. The best vulcanizate was given by litharge, the decreasing order of activity of the other oxides following the decreasing lead content consequent on an increasing oxygen content. The oxy salts displayed small and in most cases negli-

TABLE III

Oxide	Time of Heating (Min. at 150° C.)	Tensile Strength (Lbs. per Sq. In.)	Modulus at 500% Elongation (Lbs. per Sq. In.)	Comments on the Vulcanization
Aluminum (Al_2O_3)	80	No cure
Antimony (Sb_2O_3)	80	No cure
Arsenic (As_2O_3)	80	Just insoluble in benzene
Barium monoxide (BaO)	7	1670	300	Black vulcanizate, no bloom, swells only slightly in benzene
	13	1521	308	
	24	1300	300	
Barium peroxide (BaO_2)	15	889	200	Color not as dark as monoxide. No bloom
	45	920	550	
	80	940	440	
Bismuth (Bi_2O_3)	80	No cure
Cadmium (CdO)	15	Slight cure, low tensiles
	45	250	121	
	80	200	151	
Calcium (CaO)	15	81	...	Slight cure, very high swelling, maximum in solvents
	45	237	145	
	80	260	175	
Chromium (CrO_3)	80	No cure
Chromium (Cr_2O_3)	80	No cure
Cobalt (Co_2O_3)	40	Very slight cure
Cupric (CuO)	15	60	...	Slight cure
	45	74	...	
	80	
Cuprous (Cu_2O)	15-80	Very slight cure
Ferrous (FeO)	45	150	140	Slight cure
	80	245	160	
	80	
Ferric (Fe_2O_3)	80	No cure
Ferroso-ic (Fe_3O_4)	80	Very slight cure
Litharge (PbO)	25	1313	300	Well vulcanized
Red lead (Pb_3O_4)	45	840	522	Well vulcanized
Lead peroxide (PbO_2)	45	507	230	Vulcanized
Magnesium (MgO)	80	250	...	Cure
Mercuric (HgO)	15	400	100	Definite cure
	45	430	175	
	80	125	...	
Nickel (NiO)	80	Very slight cure
Phosphorus (P_2O_5)	80	50	...	Slight cure
Potassium (KOH)	80	150	...	Slight cure; black
Silicon (SiO_2)	80	Very slight cure
Silver (Ag_2O)	20	500	...	Good cure; porous
Sodium (NaOH)	80	105	...	Black
Stannic (SnO_2)	80	50	...	Very slight cure
Stannous (SnO)	80	Slight cure
Strontium (SrO)	15	414	...	Definite cure
	45	422	...	
	80	250	...	
Titanium (TiO_2)	80	No cure
Zinc (ZnO)	80	No cure
Carbon (CO_2)	60	No cure
Nitrogen (NO_2)	60	Definite surface cure
Sulfur (SO_2)	60	No cure

gible activity. No compound which does not contain oxygen has been found to activate vulcanization by dinitrobenzene.

As the oxides of lead were found to be the most active it was expected that the oxides of other metals would also be the most likely compounds for activating vulcanization by dinitrobenzene.

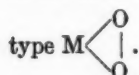
Influence of Metallic Oxides.—A large master-batch of 100 parts of pale crepe rubber and 6 parts of *m*-dinitrobenzene was made. This was divided into the necessary number of portions and 15 parts of metallic oxide were added to each. Samples were press-heated at 150° C. for various times. Vulcanization was detected by the action of benzene, and where possible the tensile properties were examined. The results are given in Table III.

The apparatus found most convenient for examining the vulcanizing tendencies of certain mixes in gases consisted of a small test tube fitted inside a larger one; the outer side of the smaller tube had a thin film of rubber formed on it by dipping into a solution of the desired mix. The space between the two tubes was then filled with the gas and the whole apparatus heated in a steam pan.

The activation of dinitrobenzene vulcanization by metallic oxides may thus be summarized: Many oxides other than those of lead are capable of inducing vulcanization. The oxides giving the highest tensile strengths are lead monoxide and barium monoxide, the latter giving by far the quickest cure.

The activity of the oxide as evidenced by the physical properties of the vulcanizate appears to bear no direct relation to the atomic number of the element. When plotted graphically a series of peaks is obtained (Fig. 1). Elements belonging to any given group of the periodic table occupy corresponding positions in relation to the peaks. If such corresponding points are selected they give the curves shown in Fig. 2; in the case of electro-positive elements, increasing atomic complexity gives increased activity, whereas elements yielding acidic oxides show diminishing activity with increasing atomic weight.

Oxides of divalent metals of the type $M=O$ are found to be much more active than those of monovalent metals of the type $M-O-M$ or of divalent metals of the



The power of an oxide to activate vulcanization by dinitrobenzene shows no relation to its ability to accelerate vulcanization by sulfur.

Organic Compounds.—It was considered that in all probability some organic compounds would be capable of activating vulcanization in the same way as the metallic oxides. Various types of organic compounds, including many containing oxygen bound in different ways, were tried in the base mix, 10 parts of the organic compound being added in each case.

Accelerator A-19, benzothiazyl disulfide, aniline, aniline sulfate, benzamide, mercaptobenzothiazole, diphenylamine, diphenylguanidine, furfuraldehyde, glucose, nitrobenzene, and Vulcafor resin were tried without success, and acetone, acetic acid, acetic anhydride, carbon dioxide, cyclohexanone, ether, ethyl alcohol, formaldehyde, and methyl alcohol were tried in the gas apparatus with the same result.

Very slight signs of vulcanization were given by mixes containing acetamide, phenol, and *m*-cresol, whereas the only substances which were found to activate vulcanization to a substantial degree were lead and barium acetates and urea.

The activation of dinitrobenzene by organic compounds may be summarized thus: Urea is the only organic compound found to activate vulcanization to a large extent; this vulcanizate was porous, hygroscopic, and had a golden color.

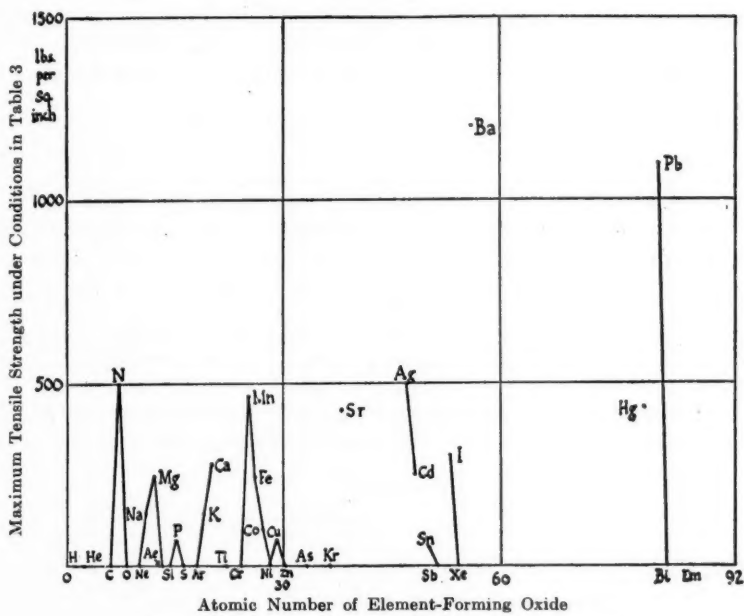


Figure 1—Activating Effect of Oxides in Vulcanization

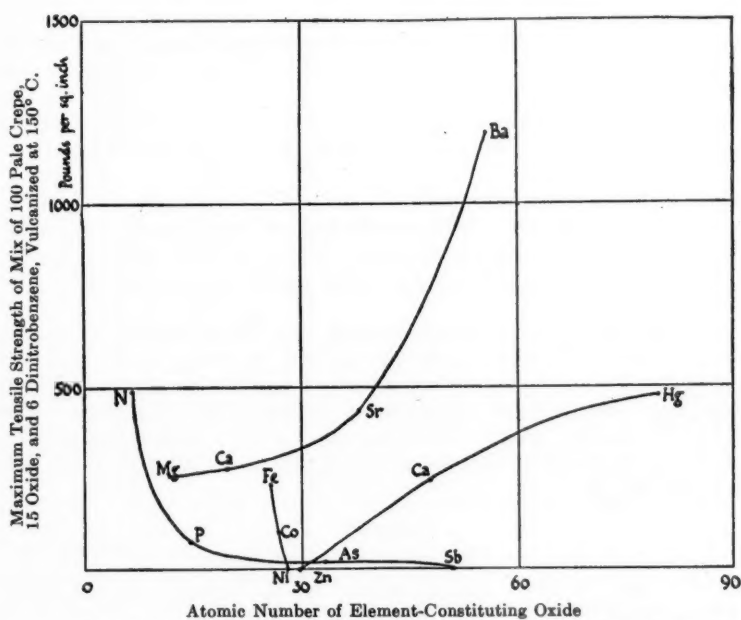


Figure 2—Activating Effect of Groups of Oxides in Vulcanization

The effect of *m*-cresol and phenol took the form of a reduction of tackiness rather than definite vulcanization. Lead and barium acetates probably owe their action to the presence of the respective oxides either as impurities or as products of thermal decomposition.

The Effect of Serum Substances in Rubber on the Rate of Vulcanization and Properties of the Vulcanizate.—Distinct differences of strength were usually observed between vulcanizates made from pale crepe and smoked sheet; the latter generally (although not invariably) gave slightly quicker cures and higher tensile strength.

In view of the foregoing results, it was thought possible that these variations might be attributed to differences in quantity and nature of serum substances present. It is also possible that substances added to the rubber by smoking may be responsible for at least a part of the variations.

Water-soluble Substances in Crepe Rubber.—A sample of crepe was extracted by heating in distilled water four times for periods of 15 minutes at 150° C. The rubber was dried in air at room temperature before use. With the base mix of 100 parts of rubber, 10 parts of litharge, and 6 parts of dinitrobenzene, the following variations were observed after vulcanizing for 27 minutes at 145° C.

TABLE IV

Rubber	Mean (of 3) Tensile Strength (Lbs. per Sq. In.)	Maximum Tensile Strength (Lbs. per Sq. In.)
Smoked sheet rubber	1334	1380
Pale crepe rubber	932	1048
Water-extracted crepe rubber	147	173

On evaporating the extract to dryness a resinous deposit was obtained. The small quantity was insufficient for more than a few tests; negative tests were given for sulfur (which may have been added as sodium sulfite) in the form of sulfite, sulfate, sulfide, or in organic combination.

The chief serum substances known to be present in raw rubber are mineral matter, sugars, resins, fat acids, and proteins. In addition to these, in the case of smoked sheet there may be phenols.

It is clear from the results in Table IV that some part of these substances is water-soluble, and that this part contains some substances which assist vulcanization with dinitrobenzene.

Mineral Matter.—Phosphorus, calcium, magnesium, and potassium oxides and hydroxides have been shown to activate this form of vulcanization slightly (Table III); the mineral matter often present in raw rubber is therefore likely to activate vulcanization slightly, but certainly not to the extent required to explain the observed differences.

Sugars.—Van Dillen (*Arch. Rubbercultuur*, 6, 263 (1922)) stated that the decomposition product of the heterosaccharides present in rubber is either glucose or fructose. Glucose was selected to study the effect of sugars contained in raw rubber.

Glucose was found incapable of activating vulcanization in the absence of some other activator, and the addition of 1 per cent of glucose to the litharge base mix did not change its tensile properties after vulcanizing for 27 minutes at 145° C. (Table V and Fig. 3).

TABLE V

Mix	Mean Tensile Strength in (Lbs. per Sq. In.)	Maximum Tensile Strength (Lbs. per Sq. In.)	Modulus at 500% Elongation (Lbs. per Sq. In.)
Crepe rubber	1020	1040	265
Crepe + 1% glucose	1046	1100	265

Resins.—Wood-rosin and shellac, as typical natural resins, and "Vulcafor resin" as a similar synthetic product, were employed to represent the resinous components of the serum. One per cent of these substances was added to the litharge base mix, yielding the results in Table VI.

TABLE VI

Mixing	Time of Cure (Minutes)	Temp. of Cure (° C.)	In Pounds per Sq. In.		
			Mean Tensile Strength	Maximum Tensile Strength	Modulus (500%)
Pale crepe rubber	40	141	965	1111	200
Crepe + 1% rosin	40	141	411	478	130
Crepe + 1% shellac	40	141	859	889	200
Smoked sheet rubber	40	141	400	400	180
Smoked sheet + 1% rosin	40	141	410	444	170
Smoked sheet + 1% shellac	40	141	413	430	160
Pale crepe rubber	27	145	1024	1048	210
Crepe + 1% Vulcafor resin	27	145	1590	1622	330

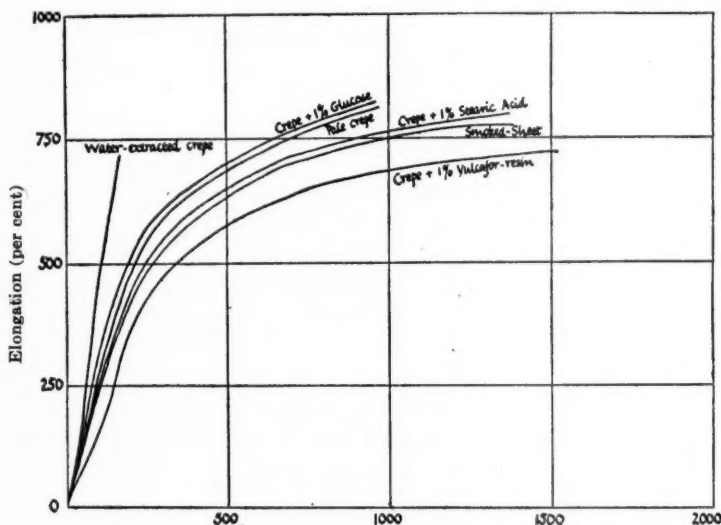


Figure 3—Load (lbs. per sq. in.)

It is shown by the results in Table VI that further addition of natural resins to smoked sheet rubber has no effect, but to unsmoked rubber the addition of such resins is detrimental (Fig. 4).

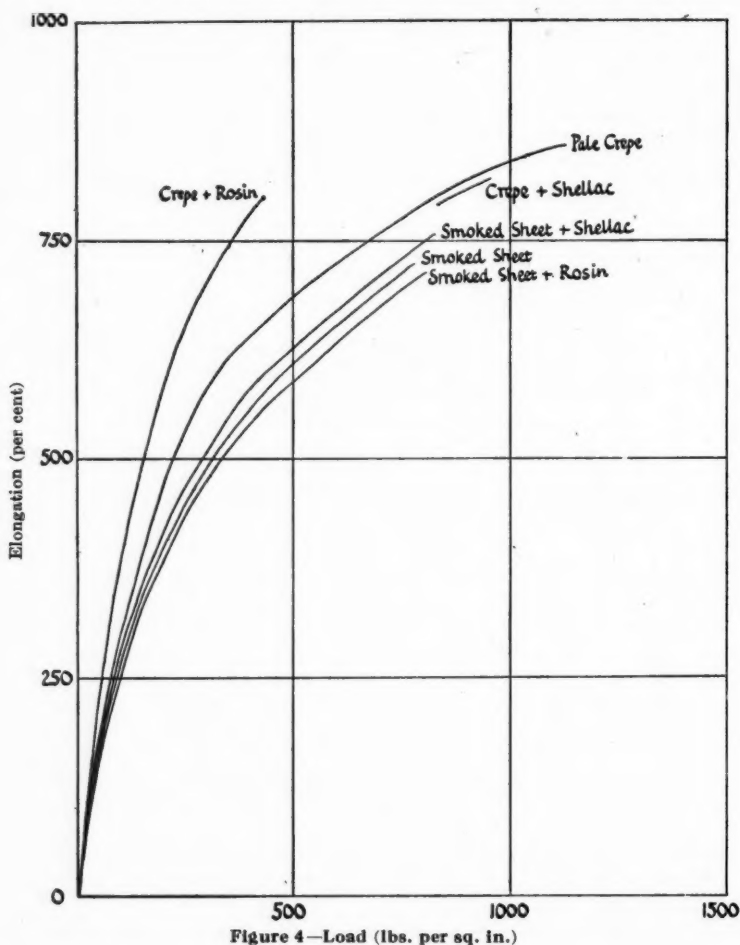
The effect of the synthetic resin bears no relation to that of the natural resins, although the above results show that this preparation is an accelerator for this type of vulcanization.

The Fatty Acids.—Stearic acid has been identified as a serum substance and was therefore chosen as representative of its class. To the base mix containing litharge, 1 per cent of the acid was added and samples were vulcanized for 27 minutes at 145° C.

TABLE VII

Mix	Mean Tensile Strength (Lbs. per Sq. In.)	Maximum Tensile Strength (Lbs. per Sq. In.)	Modulus (Lbs. per Sq. In.)
Pale crepe rubber	932	1048	200
Crepe + 1% stearic acid	1232	1325	245
Smoked sheet rubber	1338	1380	250

It is thus shown that stearic acid increased the tensile strength of vulcanizates prepared from pale crepe rubber. It has been suggested that this improvement is



due to the solubility of lead stearate; it is also of interest to note that lead acetate, which is completely soluble, gives results inferior to those obtained with litharge. Lead acetate, however, gives rise to acetic acid on heating. It has also been found that by including 1 per cent of stearic acid in other mixings, more uniform products are obtained.

Proteins.—Casein and gelatin were considered to be typical proteins, and the effect of adding 1 per cent of these to the litharge base mix was investigated. Vulcanization was carried out at 145° C.

TABLE VIII

Mix	Time of Cure (Min. at 145° C.)	Mean Tensile Strength (Lbs. per Sq. In.)	Maximum Tensile Strength (Lbs. per Sq. In.)	Modulus at 500% Elongation (Lbs. per Sq. In.)
Crepe rubber	15	421	574	180
	30	1130	1450	200
Crepe + 1% casein	15	580	600	185
	30	980	1000	220
Crepe + 1% gelatin	15	480	525	200
	30	1112	1275	220

The effect of protein matter as shown by these results (Fig. 5) is only such as might be explained on the supposition that their particles influenced the stress-strain curve by virtue of their unsuitable size or bad dispersion.

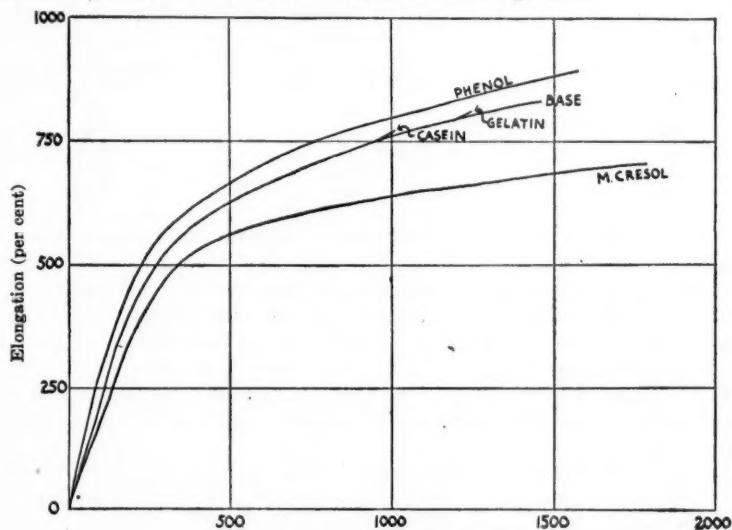


Figure 5—Load (lbs. per sq. in.)

Smoke.—Among the substances stated to be present in smoke are phenol and the cresols; these substances are likely to be added to the rubber during normal smoking.

The effect of adding 1 per cent of phenol and 1 per cent of *m*-cresol to the litharge base mix was investigated after vulcanizing for 15 and 30 minutes at 145° C. (see Table IX and Fig. 5).

TABLE IX

Mix	Time of Cure (Minutes)	Tensile Strength		
		Mean (Lbs. per Sq. In.)	Maximum (Lbs. per Sq. In.)	Modulus (Lbs. per Sq. In.)
Crepe rubber	15	427	574	160
	30	1130	1450	280
Crepe + 1% phenol	15	385	574	180
	30	1326	1594	210
Crepe + 1% <i>m</i> -cresol	15	955	1100	220
	30	1659	1721	360

It appears that both phenols when added to crepe rubber have a beneficial influence on the vulcanizing properties, the products being considerably stronger after 15 and 30 minutes' vulcanization. The figures also indicate an earlier "set-up" in the case of the stock containing cresol.

In view of the improvement shown, it seems likely that the retardation of sulfur cures by phenol-formaldehyde resins attributed by Naunton and Siddle (*India Rubber J.*, **82**, 535 (1931)) to the presence of free phenols might be overcome by the use of dinitrobenzene as the vulcanizing agent for the rubber phase. It is proposed to report on this at a later date.

As several types of auxiliary substances were found to improve the physical properties of the vulcanizate, it was decided to examine the effect of including all the beneficial substances in a crepe mix.

The following mix was made: 100 parts of pale crepe rubber, 10 parts of barium oxide, 6 parts of dinitrobenzene, 1 part of *m*-cresol, 1 part of stearic acid, and 1 part of Vulcafor resin. Samples vulcanized at 150° C. were black and rather porous, and gave the results in Table X when tested in the Schopper machine.

TABLE X

Cure (Minutes)	Tensile Strength (Lbs. per Sq. In.)	Modulus at 600% (Lbs. per Sq. In.)
5	1750	498
10	1620	494
15	1630	498
20	1580	493
25	1080	490

The stock obviously vulcanized very rapidly, showing the best tensile strength after only 5 minutes' heating. The cure displayed a "plateau effect," there being only slight diminution in strength with considerable overcure. It is remarkable that the modulus figures remain almost constant, a fact which suggests that this vulcanizate would probably be particularly stable towards heat during service. Even though these samples were porous, their tensile strengths are comparable with that of rubber vulcanized by sulfur, and it is almost certain that the quality of the product could be materially improved by suitably adjusting the mix and the vulcanizing conditions.

The Aging of Dinitrobenzene Vulcanizates.—The aging products of several different mixes were examined by test samples before and after three days' aging in a Geer oven at 70° C. The results are given in Table XI.

The fall in tensile strength of all vulcanizates during aging was considerable. Samples 1 and 2 and 8 and 9 are instructive; when added to mixes containing litharge and made from pale crepe rubber, 1 per cent of Nonox gives a weaker vulcanizate. During the three days' aging, the Nonox vulcanizates apparently "reverted"; this was shown by the use of solvents, which brought about complete dispersion. On the other hand, when included in a mix made from smoked sheet containing barium oxide as an activator, Nonox caused not only an increase of approximately 5 per cent in the tensile strength of the vulcanizate, but also a marked improvement in its aging properties, the fall in tensile strength on aging being approximately 40 per cent less than in the case of the base mix.

By comparing samples 1 and 7 it is seen that although manganese dioxide activates vulcanization with *m*-dinitrobenzene it is detrimental to the aging of the vulcanizates as in the case of sulfur vulcanizates.

Experiments on natural aging, undertaken with a view to showing the validity of the results of accelerated aging tests, indicated that samples exposed to the sun

and air for nine months were not as seriously affected as those submitted to the aging test for three days. Exact correlation has not so far been attempted. The blooming of the naturally aged samples was very great, and continued throughout the period of aging; partially aged samples, after cleaning, again became coated with a deposit after a few days. This phenomenon was not observed during the accelerated aging tests because at 70° C. the vulcanizing agent was distinctly volatile, and its characteristic odor could be detected with ease.

TABLE XI

AGING

	Cure Min.	°C.	Before Aging		After Aging	
			Tensile Strength (Lbs. per Sq. In.)	Tensile Product ÷ 10 ⁴	Tensile Strength (Lbs. per Sq. In.)	Tensile Product ÷ 10 ⁴
Mix						
1. Crepe rubber 100, litharge 10, D. N. B. 6	31	141	1205	118	500	2
2. Mix 1 + 1% Nonox S	31	141	400	38
3. Smoked sheet 100, red lead 10, D. N. B. 6	70	141	1835	147	500	37
4. Smoked sheet 100, lead dioxide 10, D. N. B. 6	70	141	750	71	50	3
5. Crepe 100, PbO 10, BaO 10, D. N. B. 6, lead acetate 2	17	141	1606	131	444	32
6. Mix 5 + 1% of Nonox	17	141	1500	105	263	11
7. Crepe 100, PbO 10, manganese dioxide 10, D. N. B. 6	31	141	300	24	0	0
8. Smoked sheet 100, barium monoxide 10, D. N. B. 6	10	151	1926	160	750	58
9. Mix 8 + 1% Nonox	10	151	2050	190	1184	112

As the oxides of lead and barium are the only practical efficient activators, and other oxygen compounds of the metals and of carbon have a relatively small effect, the view has been formed that oxygen is the essential activating element, but that this oxygen must be in some suitable condition before such activation can occur. Whether this condition depends on the type of atomic combination, on the electric charge residing on the ions, or on some other energy function of the atoms remains undetermined, but it is certain that a very interesting field of fundamental research has been entered. The exact relation between this action of oxygen and those actions associated with mastication of crude rubber and aging of vulcanized rubber is still a matter for speculation and future work of a very far-reaching character.

The author would like to express his sincere appreciation of the assistance and advice given by B. L. Davies, under whose guidance the investigation was made.

The Properties of Rubber Cements

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Rubber cements used in factories manufacturing rubber goods consist of rubber-solvent dispersed systems. They usually contain, in addition to rubber, various pigments, softeners, curing agents, etc. The smoothness and thickness of the films deposited, the readiness with which the films break over small apertures in dipped objects, the viscosity, and the stability of the cements as liquid systems are characteristics which affect their utility. The purpose of this paper is to present a

summary of empirical data relating such working properties and important variables in composition. Whereas there is in the literature much data on the properties of extremely dilute rubber solutions, obtained in the course of theoretical researches, little information is available concerning the much more concentrated cements used commercially.

Of the classical properties of liquids only viscosity will be discussed in this paper.

Viscosity

A rubber solution is not a truly viscous system. Newton's equation defining viscosity as the constant ratio of shearing stress to rate of shear fails to describe its flow characteristics, because in a rubber solution the ratio of shearing stress to rate of shear varies with the shearing stress.¹ Einstein's equation relating the apparent viscosity of a colloidal solution

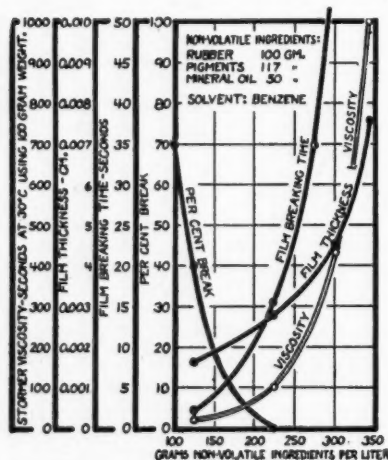


Figure 1—Relation of Various Properties of a Rubber Cement to the Concentration of Non-Volatile Ingredients

to the viscosity of the medium for the case of a dilute suspension of spherical particles also does not hold.² Numerous other equations have been proposed.³

Despite the fact, however, that viscosity measurements in themselves possess little fundamental significance, the term viscosity is widely used to describe in a general way the flow characteristics of cements. The property is suggestive of others of more direct utility, such as the thickness of film deposited upon a dipped article, but it does not take the place of actual measurement of these. In practical use, viscosity is measured primarily to check uniformity. In experimental development it is usually of secondary importance. The manner in which apparent viscosity changes with concentration of solids for a commercial cement, as well as the relation of viscosity to other properties discussed in this paper, are shown by Fig. 1.

Aside from concentration, the degree of mastication of rubber is perhaps the most important factor in the control of viscosity, the viscosity of cements being

enormously reduced merely by prolonged milling of the rubber compound. Viscosity also may be reduced by the addition of non-solvents, as ethyl alcohol, and by certain chemicals. Whitby and Jane⁴ found the viscosity of dilute rubber solutions to be reduced by small amounts of acetic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, diethylamine, piperidine, benzylamine, quinine, isobutylamine, etc., but not by aniline; in this laboratory similar results were obtained with cements of commercial concentrations.⁵ Different solvents may give solutions of widely different viscosities. For 1 to 2% solutions of fine Para an order of decreasing viscosity given by Gaunt⁶ is: benzene, chloroform, petrol; for Castilloa: chloroform, benzene, petrol. For factory-type cements of 10 to 30% concentration, in studying film breaking (assumed to be an approximate measure of viscosity), the writer⁷ found the order: benzene, V M & P naphtha, ethylene dichloride; or V M & P naphtha, benzene, ethylene dichloride, depending on the concentration. In general, for any given concentration of rubber compound, viscosity is reduced by increased pigment loading, due to less rubber and consequently less structure; but certain specific pigments, as carbon black,⁸ or magnesia, cause increase in viscosity. Similarly, specific chemicals cause increase in viscosity, probably by a process of incipient gelling. Water increases the viscosity of cements when added in comparatively small amounts, but the presence of mere traces of water in rubber apparently reduces viscosity. Thus a sample of rubber dried for one year over sulfuric acid when made up to a 5% solution in xylene formed a gel; whereas an identical sample of rubber, but which had been kept for one year over water, when made up to a 5% solution in xylene gave a very limpid cement. The permanence of these various effects and the importance of relative amounts of chemicals have not been sufficiently studied.

Film Thickness

The thickness of the film deposited from a cement upon a dipped object is important not only because of the effects on the adhesive or protective value, but indirectly because of its relation to the colloid mechanics of drying films to be discussed later under film smoothness.

A satisfactory measure of film thickness can be obtained by dipping a small iron panel into the cement to a definite depth and withdrawing carefully at a standard rate. When the solvents have all escaped from the deposited film, its weight and hence its average thickness can be determined by difference. With this simple test the experimenter may often obtain a better idea of the quality of a cement than with a viscosity measurement.

The film thickness deposited upon dipped panels increases with concentration (Fig. 1), decreases with mastication, and changes with temperature and humidity for any given cement. A large number of qualitative observations by the writer indicate that in general solvents which evaporate quickly give thicker films than solvents which evaporate slowly. Non-solvents reduce film thickness, probably because they reduce viscosity.

Film Breaking

In dipping cements, the ease with which wet films break across small holes in perforated objects often is important. The film-breaking tendency may be easily measured as "film-breaking time," in seconds required for a standard vertical film to break, or as "percentage break," the number of films breaking of 100 standard films formed over small holes in a perforated panel.

The "standard film" used in experiments by the writer is that formed over a small round hole (0.63 cm. in diameter) centered 0.63 cm. from the end of a $5 \times 12.5 \times$

0.079 cm. iron panel. Panels are dipped to a depth of 5 cm. in cements free from air bubbles or scum, withdrawn slowly at a standard rate, and the time measured from the instant of withdrawal of the film through the cement surface. For the measurement of "percentage break," small aluminum panels 0.157 cm. thick carefully perforated with 100 holes 0.48 cm. in diameter, evenly spaced on 0.073 cm. centers, are employed.

Film-breaking is probably influenced by film strength (*i. e.*, cohesive strength), surface tension, internal friction or viscosity, and evaporation rate. These effects are rapidly changing as the solvent escapes, and the mechanics involved are undoubtedly extremely complicated, but film-breaking is the net result. Aside from its direct utility, film-breaking, like viscosity and film thickness, is a measure of consistency, and this is illustrated by the similar manner in which these properties vary with concentration, as shown in Fig. 1.

The film-breaking tendency of a cement may be greatly increased by the addition of a non-solvent. In studying comparative effectiveness of various non-solvents in causing film breaking, the writer has found the most satisfactory non-solvent for benzene cements to be isopropanol; for V M & P naphtha cements, isopropanol; for ethylene dichloride cements, butanol.⁷ While non-solvents improve film-breaking, they decrease film thickness at the same time, and these effects must be compensated by simultaneous changes in concentration of solids and degree of mastication of rubber.

Film Smoothness

For many reasons it is desirable that deposited rubber films be smooth, and that the pigments be distributed uniformly. One of the less obvious effects of poor pigment distribution is encountered in curing cements where the curing rate of the film may be greatly reduced because of agglomeration of sulfur particles. Agglomeration causes decrease in effective sulfur concentration, and for this reason more sulfur is ordinarily used in rubber compounds for cements than in corresponding compounds which are cured as batch stock, without prior addition of solvent. Poor pigment dispersion may be the result of poor mixing of the rubber batch, and agglomeration of sulfur may occur through crystallization in solution, but redistribution of pigments always and inevitably occurs during the evaporation of the solvents from a film, because of vortex action.

Vortex action in color varnish has been described by Bartell and Van Loo.⁹ A vortex is a tiny crater in which the solvent is boiling up in the center and flowing outward uniformly in all directions, and these vortices space themselves evenly, as hexagons, over all the surface of a film from which the solvents are escaping. The obvious effect of this violent motion in the fluid medium is transportation of particles; and under the microscope, in rubber cement films from which the solvent is evaporating, the pigment particles may easily be observed moving outward from and piling up around the vortices.

Ordinarily the particles of largest size, and at the same time least gravity, are those of sulfur; and these have the greatest tendency to pile up. If high-boiling solvents, or heavy petroleum oils such as Nujol, are present in the film, "secondary flow" is made possible, and here again sulfur has the least tendency to flow back into the film and redistribute itself. The size of the vortices depends on film thickness, particle size, and solvent, because these influence fluidity. If solvent mixtures are well chosen and fine particle size pigments used, the effect of vortex action can be greatly reduced.

Cement Stability

One of the nuisance properties of cements is gelling. Some cements gel and some do not. Some gel quickly, and some require months. Gelling may occur for a number of reasons, and not all gelled cements look alike. Whether these differences are due to differences in kind of gelling, or merely to differences in degree, is not known. The words gelling, livering, curing, and lobbering have been used rather loosely to indicate the physical condition of cements which have "set up." Even the physical differences implied by these words are not clear; chemical differences, if any exist, are not understood. In terms of structure however, the mechanism of gel formation is probably one of interlocking of contiguous rubber fibers or molecules through some kind of chemical bond.

Spontaneous gelling of cements, at room temperatures, may be caused by ultra-accelerators. It may also be caused by increase in effective accelerator or sulfur concentration as a result of reduction of pigment loading in the rubber compound.

Many chemicals that are not vulcanizing agents cause gelling. These cases may be explained by polymerization of rubber, activation of accelerator already present in the cement, or by specific effects on the swelling power of the solvent. Similarly, certain chemicals prevent gelling in some cases. An important example of the effect of chemicals on cement stability is afforded by the case of the chlorinated solvents.

Chlorinated solvents sometimes cause gelling and sometimes prevent it, and these effects may be due to traces of chlorine or hydrogen chloride formed by decomposition of the solvent. In many cases the changes in the cement evidently are caused by chemical action of chlorine or hydrogen chloride on the accelerator present. Thus chlorinated solvents often cause gelling of cements accelerated with certain aldehydeamine reaction products, and it is known that chlorination of certain members of this class of accelerators greatly increases their activity.¹⁰ As an example of an opposite effect, Thiollet¹¹ found that gelling of cements accelerated with tetramethylthiuram disulfide or with a mixture of tetramethylthiuram monosulfide and mercaptobenzothiazole was prevented by replacing benzene or gasoline with ethylene dichloride, but that the ability of the film to cure was destroyed at the same time. In addition to this point, however, Thiollet observed that after a few days the apparent viscosity of the ethylene dichloride cements began to decrease in contrast with the corresponding benzene and gasoline cements. Obviously, the chlorinated solvent, probably through its decomposition products, has a profound effect not only on the accelerator, but on the rubber as well.

Non-solvents, such as isopropanol, in certain cements induce gelling. This effect seems due to increase in effective total solids concentration of the cement by solution of a portion of the solvent in the non-solvent. The granular appearance of gelled benzene-isopropanol cements supports this explanation in that an incipiently discontinuous system is indicated.

Oxygen may either reduce viscosity, or apparently cause gelling. These contradictory effects are possibly explainable on the basis of the amounts of oxygen present. Traces seem to cause gelling and may be assumed to promote a "sulfurless" type of contiguous chain linkage, or vulcanization, through free valences. The fact that antioxidants do not prevent gelling seems to lend support to this view.¹² Appreciable amounts of oxygen on the other hand, perhaps by decreasing the length of the rubber molecules,¹³ reduce the gelling tendency.

In curing cements pigments may promote gelling because of incipient vulcanization promoted by the higher temperature of milling. When this effect is not pro-

duced, large volumes of pigments may on the other hand inhibit gelling, both by increasing breakdown of the rubber and by their dilution effect.

Reduction of concentration of the rubber compound in a cement always tends to prevent gelling. This is of course an effect resulting from further expansion of the gel structure. In very thick cements, however, this effect of expansion may be offset by the solvent functioning as a vehicle for the sulfur and the accelerator. By facilitating contact between rubber and curing agents, a small amount of solvent may cause a system to cure more quickly than if no solvent were present.¹⁴

Other Properties

Drying time is controlled directly by evaporation rate through choice of solvents, indirectly by temperature and humidity.

Pigment settling is reduced by using pigments of fine particle size, by improving pigment dispersion, by powerful solvents such as kerosene, and by protective colloids as triethanolamine soaps. Settling is promoted by non-solvents such as isopropanol.

The brushing, spreading, and spraying qualities of cements are improved by increased mastication, by using high-boiling solvents, and by incorporation of proper amounts of resins and pigments.

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The Behavior of Ebonite towards Organic Liquids

J. R. Scott

INTRODUCTION

The behavior of ebonite towards oils, gasoline, benzene, and numerous other technically important organic liquids has not been studied so fully as the behavior of soft vulcanized rubber towards such liquids. This is doubtless due to the extensive applications, actual or potential, of soft rubber in situations involving exposure to organic liquids, especially gasoline and mineral oils, and to the fact that the production of soft rubber to withstand such liquids is one of the most difficult problems confronting the rubber manufacturer.

Although ebonite is much less widely used than soft vulcanized rubber, its unique properties render it invaluable for a variety of purposes, so that it is important that as much as possible should be known about its properties. Among those properties of ebonite that have received comparatively little attention is its behavior towards organic liquids. Nevertheless, this is of considerable importance, as is evident on considering the extensive use, for instance, of ebonite pipes, valves, pumps, containers, and tank linings in the chemical industry, and also its use as an electrical insulating material in situations which may involve contact with lubricating or insulating oils. In addition to these major uses there is a host of minor ones, such as centrifuge linings, spinnerets for rayon, ebonite-covered rollers for various industries, medical syringes and atomizers, and ebonite-bonded abrasives, all of which may be used in contact with an organic liquid or material of a greasy nature. Even the familiar ebonite stems of tobacco-pipes are constantly subjected to the action of nicotine and tarry matter.

It is thus evident that a knowledge of the behavior of ebonite towards organic liquids is important in relation to many of its uses, and yet the amount of exact information available on this subject is surprisingly small. A great many of the references in the literature are confined to general statements that "ebonite tends to soften and swell in hot oil," or "ebonite is extraordinarily resistant to oils," or "ebonite is attacked by most rubber solvents:" statements that are often as inaccurate as they are vague.

Boiry (*Caoutchouc & gutta-percha* 20, 12,010 (1923)) examined the swelling in toluene, xylene, gasoline, "petroleum," nitrobenzene, and phenetole, of a rubber-sulfur (65:35) mixing, vulcanized to different degrees, and noted how the influence of increasing combined sulfur content on swelling varied according to the nature of the liquid. Webster (*Research Assoc. Brit. Rubber Manufs. J.*, 3, 15, 27 (1934)) obtained time-swelling curves for ebonite in benzene, and drew attention to the slowness of the absorption. Porritt and Scott (*India Rubber J.*, 86, 253 (1933)) and Scott (*Research Assoc. Brit. Rubber Manufs. J.*, 5, 2 (1936)) made tests on various loaded and unloaded ebonites in benzene; they confirmed Webster's observations and showed how increasing combined sulfur content reduced the amount of liquid absorbed and the rate of absorption. Ariano (*Il Politecnico*, 1931, No. 12) found that heavily loaded ebonite swelled much less in benzene than unloaded ebonite, and noted the effect of swelling on physical properties.

In view of the scantiness of published information, a study of the behavior of ebonite towards organic liquids has been undertaken by the Research Association of British Rubber Manufacturers ancillary to the larger program on bonite which is being carried out jointly with the British Electrical and Allied Industries Research Association. Although this work is still far from complete, it is thought that an account of the results so far obtained will be of interest.

EXPERIMENTAL

1. Methods

The ebonites examined were prepared from washed smoked sheet and sulfur only, and vulcanized in molds at 155° C. to give sheets 5 to 5½ mm. thick. For the swelling tests, specimens about 2 cm. square were cut from these sheets and immersed in the liquid contained in a stoppered bottle kept in the dark at constant temperature. From time to time the specimen was removed, wiped dry with filter paper, and weighed. The increase in weight was taken as the weight of liquid absorbed, and from this, together with the original weight of the specimen, its density and the density of the liquid, the swelling was calculated as volumes of liquid absorbed by 100 volumes of the original sample, that is, as percentage increase in volume.

As any extraction of soluble matter by the liquid introduces an error into this method of measuring swelling, the amount so extracted was determined in some of the experiments and in certain cases appropriate corrections were applied to the calculated swelling.

2. Experiments with Various Liquids

The first set of experiments was made to examine the action of liquids of various chemical types. Ebonite samples Nos. 3 and 12 (see Table V) were used, the former being fully vulcanized to the stage corresponding to C_8H_8S , and the latter having a combined sulfur content approaching the lower limit for a satisfactory unloaded ebonite. Swelling tests were carried out at 34° C. with the liquids shown in Table II.

(i) *Soluble Matter Extracted.*—In the experiments with petroleum ether, cyclohexane, decalin, xylene, alcohol, acetone, and ethyl acetate, the liquid remaining at the end of the experiments, which lasted anything from 2000 to 8000 hours, was evaporated and the residue weighed. Sample 3 in xylene gave a residue of 4.5 per cent of its original weight, but in all the other cases the residue was less than 1.5 per cent. As the extracted matter was thus always less, and usually much less, than the acetone extract (see Table V) it may be concluded that the rubber-sulfur compound is insoluble at 34° C. in the liquids named. This conclusion was confirmed by other tests with benzene and ethyl acetate (see later). As the amount of extracted matter was so small no correction was applied to the swelling.

(ii) *Swelling Results.*—In the following cases either the swelling was extremely small (less than 0.5 per cent) or else the specimen showed a slight loss in weight (not more than 0.2 per cent): sample 3 in petroleum ether, paraffin, transformer oil, cyclohexane, decalin, alcohol, glycerine, linseed oil, and castor oil, and sample 12 in paraffin, transformer oil, alcohol, glycerol, linseed oil, and castor oil.

The curves of swelling against time for the remaining experiments are shown in Figs. 1 and 2, the former giving the results for the first 300 hours and the latter the complete curves for the more prolonged experiments.

The absorption of liquid often caused the ebonite to crack, sometimes so badly that the test had to be abandoned prematurely because the sample could not

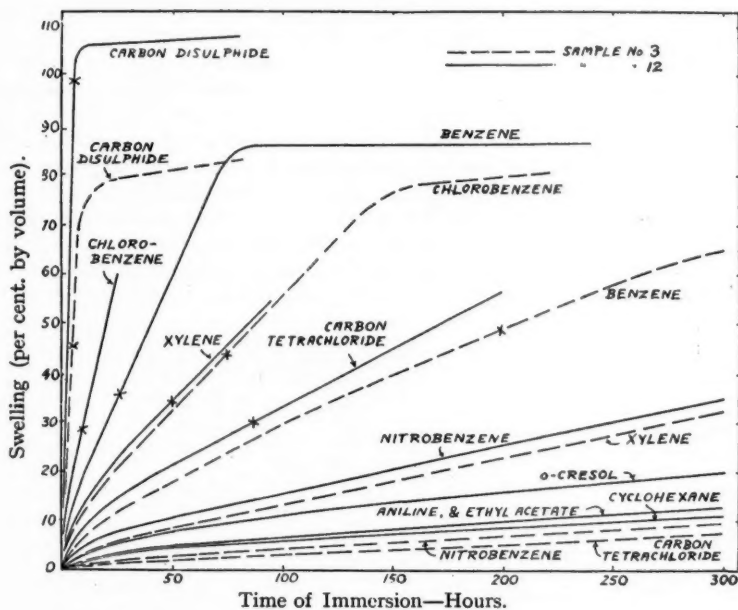


Figure 1—Swelling Curves for Ebonite in Various Liquids

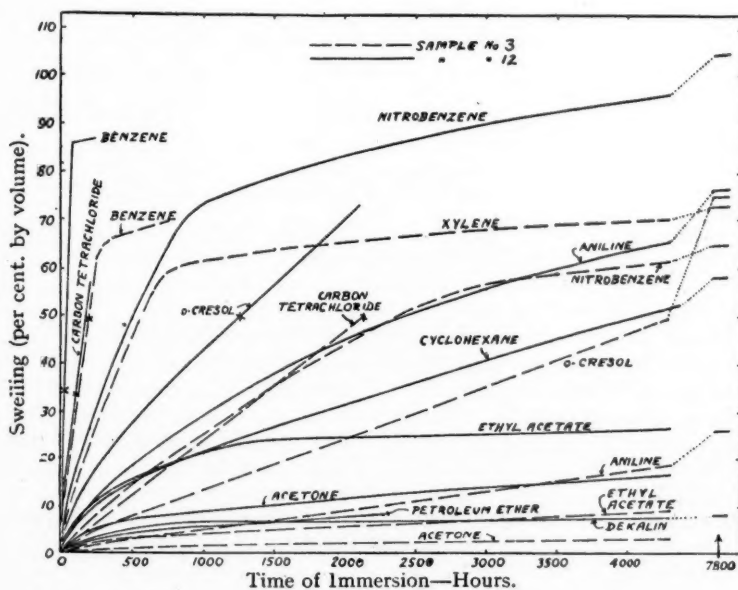


Figure 2—Swelling Curves for Ebonite in Various Liquids

be handled. The approximate time when cracking was first noticed is shown on the curve by a cross (see Figs. 1 and 2).

Many of the swelling curves are of the general type given by soft vulcanized rubber, comprising a relatively quick rise to an approximate maximum ("saturation" phase) followed by a slow uniform (or approximately uniform) increase or "increment." Where the swelling is small, say less than 10 per cent, the time-swelling curves are closely similar to the normal form characteristic of soft rubber (see Scott, *Trans. Inst. Rubber Ind.*, 5, 95 (1929); the exact shape of this curve is shown in "Rubber: Physical and Chemical Properties," by Dawson and Porritt, Fig. 59).

In other cases the distinction between "saturation" and "increment" phases is not so clearly marked, and sample 3 in carbon tetrachloride gives an almost perfectly straight line, a type of curve not hitherto observed.

TABLE I

Ebonite	Liquid	Time to Reach	Time to Reach	T/t
		0.1 of Swelling Maximum (t) Hrs.	0.7 of Swelling Maximum (T) Hrs.	
Sample 3	Nitrobenzene	150	1580	10.5
Sample 12	Nitrobenzene	20	435	21.5
Sample 3	Benzene	10	160	16
Sample 12	Benzene	2.0	42	21
N ₂ *	Benzene	16.5	205	12.5
N ₁	Benzene	8.2	120	14.5
X	Benzene	5.9	102	17.5
W ₂	Benzene	3.2	63	19.5
TY	Benzene	2.8	38	14
M	Benzene	2.35	46	19.5
R ₁	Benzene	2.35	44	19
R ₅	Benzene	1.75	42	24
W ₁	Benzene	1.4	32.5	23.5
22†	Benzene	27.0	335	12.5
15	Benzene	14.0	175	12.5
23	Benzene	11.4	175	15.5
18	Benzene	7.6	135	18
19 & 20	Benzene	7.0	116	16.5
17	Benzene	3.4	71	21
21	Benzene	2.5	67	27

* Data from Porritt and Scott (*loc. cit.*).

† Data from Scott (*Research Assoc. Brit. Rubber Manufs. J.*, 5, 2 (1936)).

Some of the curves show a feature not found with soft rubber, namely, a more or less straight portion or "flat" on the initial rising part of the curve. This is most pronounced where considerable swelling occurs, *e. g.*, sample 3 in benzene, xylene, and chlorobenzene, and sample 12 in benzene and nitrobenzene. In a swelling process where the diffusion constant of the liquid in the solid remains constant, the rate of absorption must continuously decrease. The existence of a "flat," *i. e.*, a constant rate of absorption, shows that this decrease is being counteracted by some other factor that increases the diffusion constant as swelling proceeds. The simplest explanation of this is that the swelling of the ebonite makes it more readily permeable to the liquid and so increases the diffusion constant. This would explain why the "flat" is most pronounced where the swelling is large.

Further evidence in support of this view is furnished by the following considerations. The time t required for the swelling to reach a given small fraction (say 0.1) of its maximum value will depend mainly on the diffusion constant (d) for unswollen ebonite, whereas the time T required to reach a given large fraction (say 0.7) will

depend more on the diffusion constant (D) for swollen ebonite. As the time varies inversely as the diffusion constant, the greater the ratio D/d the smaller will be the ratio T/t . The present results for benzene and nitrobenzene, the only liquids for which adequate data are available, and other results for benzene indicate that, in general, the slower the initial absorption, *i. e.*, the lower the value of d , the smaller is the ratio T/t , and hence the greater the ratio D/d (see Table I). This is what would be expected according to the hypothesis that swelling increases the diffusion constant, as the lower the diffusion constant of the unswollen ebonite, the greater (proportionately) would be the increase produced by swelling.

Another factor which must tend to accentuate the "flat" is the cracking of the specimen, which increases the surface area and hence the rate of absorption of liquid.

If the flat part of the time-swelling curve is produced backwards, it cuts off on the swelling axis an intercept which is usually about 0.15 of the swelling maximum; values of this fraction for 13 curves representing various ebonites and liquids (some from Webster, *loc. cit.*, and Porritt and Scott, *loc. cit.*) are: 0.15, 0.16, 0.13, 0.16, 0.13, 0.16, 0.17, 0.16, 0.09, 0.11, 0.14, 0.12, 0.11.

TABLE II

Ebonite Sample No.:	Swelling Maximum (Per cent by Volume)		Swelling Time		Increment	
	3	12	3	12	3	12
Petroleum ether ¹	0	3.6	3400	0	(0.2)
Paraffin oil ²	0	v. s.	0	<0.01
Transformer oil ³	0	v. s.	0	<0.003
Cyclohexane	v. s.	9	1600	<0.01	1.0 -
Decalin ⁴	v. s.	6.3	3400	<0.004	0.03
Benzene, A. R.	64	86	2500*	650*	0.85 -	0.8
Xylene ⁵	56	90†	5900*	1600*†	0.3 -	?
Carbon tetrachloride	?	73†	?	2500*	?	?
Chlorobenzene	71	80†	1350	315*†	(3)	?
Carbon disulfide	77	106	70*	40*	(8)	(2.7)
Alcohol (absolute)	0	0	0	0
Acetone, A. R.	1.3	(6)	5000	(2000)	0.05	0.23 -
Ethyl acetate	19†	24	?	(5500)	?	0.06
Glycerol	0	0	0	0
Nitrobenzene	(52)	63	26000*	6500*	(0.3)	0.65 -
Aniline	?	?	?	?	?	?
<i>o</i> -Cresol	?	95†	?	>25000*†	?	?
Linseed oil (raw)	0	0	0	0
Castor oil	0	0	0	0

Notes:

¹ A. R., free from aromatic hydrocarbons; b. p. 60-80° C.

² Lamp oil, b. p. 180-280° C., sp. gr. 0.803 at 21° C.

³ Sp. gr. 0.860 at 21° C., viscosity 37 centipoises at 21° C.

⁴ B. p. 187-193° C.

⁵ "Commercial purified."

* Time-swelling curve not of standard form; swelling time calculated from time required to reach 0.5 of swelling maximum, therefore approximate only.

† Calculated on the assumption that the straight part of the time-swelling curve is a "flat" (not an increment) and that the intercept cut off by producing it backwards to meet the swelling axis equals 0.15 of the swelling maximum.

"v. s." denotes "very small," probably less than 1.

A minus sign after the increment denotes that it decreased gradually with advancing time.

Results in brackets are approximate only.

Where the form of the time-swelling curve permits, the results are conveniently considered in terms of the three swelling constants previously defined (Scott, *Trans. Inst. Rubber Ind.*, 5, 95 (1929)), viz.: (i) swelling maximum, *i. e.*, the intercept cut off on the swelling axis by producing backwards the upper almost horizontal ("increment") part of the curve; (ii) swelling time, representing the time (in arbitrary units) required for the swelling to reach a given fraction of its maximum value; (iii) increment, *i. e.*, the increase of swelling per 100 hours on the upper, almost horizontal part of the curve. The results, so far as they are expressible in this form, are given in Table II.

(iii) *Influence of Combined Sulfur Content of Ebonite.*—Wherever measurable swelling occurs, it is lower with sample 3, which has the higher combined sulfur content, than with sample 12. On the other hand, the swelling time is always greater for sample 3 than sample 12, indicating that ebonite takes longer to reach saturation the higher its combined sulfur content. Both these observations are in accord with previous results (Boiry, *loc. cit.*; Porritt and Scott, *loc. cit.*; Scott, *Research Assoc. Brit. Rubber Manufrs. J.*, 5, 2 (1936)).

According to the hypothesis that the increment represents an increase in the liquid-absorbing capacity of the rubber due to depolymerization or disaggregation caused by oxidation (Scott, *Trans. Inst. Rubber Ind.*, 5, 95 (1929)), the rate of this depolymerization should be proportional to the ratio of increment to swelling maximum. This ratio is shown in Table III. In three out of the four cases where figures are available for both ebonites, the more fully vulcanized sample (No. 3) gives the higher figure, and a similar result is indicated by data from previous experiments (Porritt and Scott, *loc. cit.*; Scott, *Research Assoc. Brit. Rubber Manufrs. J.*, 5, 2 (1936)). This suggests that the more fully vulcanized ebonites are more liable to degradation under the influence of oxygen, a result which is confirmed by further work described below.

TABLE III

Liquid	Ratio of Increment to Swelling Maximum ($\times 100$)		Ratio of Swelling Time to Saturation Concentration ($\div 100$)		Viscosity Centipoises
	Sample 3	Sample 12	Sample 3	Sample 12	
Petroleum ether	5.5	1000	0.32
Cyclohexane	11	190	0.7
Decalin	0.4	575	1.6
Benzene	1.3	0.9	65	14	0.53
Xylene	0.5	165	35	0.56
Carbon tetrachloride	60	0.80
Chlorobenzene	4	32	7.1	0.7
Carbon disulfide	10	2.5	1.6	0.8	0.34
Acetone	4	4—*	4000	350	0.30
Ethyl acetate	0.25	280	0.38
Nitrobenzene	0.6	1—*	750	160	1.55
Cresol	>500	3.5

* Minus sign after the figure denotes a gradual decrease with advancing time.

(iv) *Influence of Nature of Liquid.*—The swelling maximum figures in Table II show that liquids consisting essentially of aliphatic hydrocarbons, *viz.*, petroleum ether, paraffin, and transformer oil, have no swelling action on sample 3 and very little on sample 12. The hydroaromatic hydrocarbons, cyclohexane, and decalin, have rather more swelling action, whereas the aromatic hydrocarbons, benzene, and xylene, swell both ebonite samples considerably. The halogen and sulfur derivatives, carbon tetrachloride, chlorobenzene, and carbon disulfide, behave like the aromatic hydrocarbons.

Among the polar compounds, those containing hydroxyl groups, *viz.*, alcohol, glycerol, and castor oil, have no swelling action, while those containing carbonyl or carboxyl groups (acetone and ethyl acetate) exert some swelling action. In view of the small swelling capacity of the lower members of the paraffin hydrocarbon series, it would appear that the introduction of carbonyl or carboxyl groups does not lower the swelling capacity, as is the case in the swelling of soft rubber.

The effect of introducing a hydroxyl or amino group into an aromatic hydrocarbon cannot be deduced exactly, but it is clear from the results for aniline and cresol that the substituent group does not by any means destroy the swelling capacity. The introduction of a nitro group slightly reduces the swelling capacity (compare benzene and nitrobenzene).

TABLE IV

RATIO OF SWELLING MAXIMUM TO THAT FOR SOFT VULCANIZED RUBBER

Liquid	Ebonite Sample 3	Ebonite Sample 12
Petroleum ether	0	0.015
Paraffin	0	v. s.
Transformer oil	0	v. s.
Cyclohexane	v. s.	0.02
Decalin	v. s.	0.012
Benzene	0.125	0.17
Xylene	0.115	0.18
Carbon tetrachloride	?	0.11
Chlorobenzene	0.134	0.15
Carbon disulfide	0.130	0.18
Acetone	0.12 ±	0.55
Ethyl acetate	0.72	1.0
Nitrobenzene	0.38	0.44
Linseed oil	0	0

Note: "v. s." denotes a very small value.

Fatty oils, as exemplified by linseed oil, appear to have no appreciable swelling action.

The swelling capacity of a liquid for ebonite does not bear a constant ratio to its swelling capacity for soft vulcanized rubber, as is evident from Table IV, which shows the ratio of the swelling maximum for ebonite to that for a rubber-sulfur (95:5) mixing of vulcanization coefficient 4.5.

The swelling capacity of hydrocarbon liquids for soft rubber decreases in the order: aromatic, hydroaromatic, aliphatic. With ebonite the decrease is greatly exaggerated, so that the hydroaromatic and aliphatic hydrocarbons have scarcely any swelling action. The fact that linseed oil behaves similarly is doubtless due to the preponderance of saturated $-\text{CH}_2-$ groups in its molecule.

It is a striking fact, in view of the powerful swelling action of aliphatic hydrocarbons on raw and soft vulcanized rubber, that when rubber is vulcanized to the stage corresponding to $\text{C}_6\text{H}_5\text{S}$ it is completely unaffected by these liquids.

The ratio of swelling of ebonite to soft rubber (Table IV) for the halogen and sulfur compounds is about the same as for the aromatic hydrocarbons. The polar liquids, acetone, ethyl acetate, and nitrobenzene, generally give higher ratios. Exact values for aniline cannot be given, but it is clear from the time-swelling curves that with sample 3 at least aniline behaves like the other polar liquids. The results of Boiry (*loc. cit.*) likewise show that polar liquids give greater ebonite/soft rubber ratios than non-polar liquids.

It may, therefore, be concluded that with increasing combined sulfur content, swelling almost always decreases, but that the extent of the decrease varies according to the liquid, and is greatest with aliphatic hydrocarbons, slightly less with hydroaromatic hydrocarbons, markedly less with aromatic hydrocarbons and halogen and sulfur compounds, and least with polar liquids. These differences may be so great that the relative swelling capacities of two liquids are reversed on passing from soft rubber to ebonite; petroleum ether and nitrobenzene are examples of this. This change in the relative affinities of the rubber for different types of liquid is evidently due to the change in its chemical nature caused by combination with sulfur.

The swelling time of ebonite (Table II) is usually greater (10 to 50 times) than that for soft rubber (Scott, *Trans. Inst. Rubber Ind.*, **5**, 95 (1929)). The only exception is carbon disulfide, which swells ebonite almost as quickly as soft rubber. Moreover, with ebonite there are greater differences between the swelling times of different liquids than with soft rubber. In the swelling of soft rubber the swelling time is smaller, broadly speaking, the less viscous the liquid, but this relationship does not apply to ebonite; thus, acetone and petroleum ether are less viscous than benzene, xylene, or carbon disulfide, and yet have higher swelling times.

The theory of liquid absorption indicates that if rubbers of different swelling maxima but equal diffusion constants are swollen in the same liquid, the swelling time is greater the higher the saturation concentration, i. e., the concentration of liquid in the fully swollen rubber. The ratio of swelling time to saturation concentration should therefore give a better idea of the diffusion constant than the swelling time itself, a low value for this ratio indicating a high diffusion constant. Table III gives the value of this ratio, calculated as $T(S + 100)/100 S$, where S and T are the swelling maximum and swelling time, respectively, together with the viscosity of the liquid. Some of the least viscous liquids such as acetone, ethyl acetate, and petroleum ether, appear from these results to diffuse most slowly. This can be explained by the influence of swelling on the rate of diffusion, already referred to [paragraph ii]. The three liquids mentioned have only a small swelling action, so that diffusion in substantially unswollen ebonite, is very slow. The fact that carbon disulfide, benzene, xylene, carbon tetrachloride, and chlorobenzene, which are at least as viscous as the above-mentioned liquids, diffuse much more quickly, and even the highly viscous nitrobenzene diffuses distinctly more quickly, can be ascribed to the stronger swelling action of these liquids, which greatly increases the permeability of the ebonite. The high ratio for decalin is due partly to its low swelling capacity and partly to its high viscosity, and the high swelling capacity of cresol is counteracted by its very high viscosity.

The conclusion to be drawn is that whereas the viscosity or some related property probably influences the rate of penetration of ebonite by a liquid, the permeability of the ebonite is so greatly increased by the absorption of liquid that the swelling capacity of the liquid is a much more important factor in determining this rate.

In view of the enormous influence of even traces of certain substances on the increment (Scott, *Trans. Inst. Rubber Ind.*, **5**, 95 (1929)) and the fact that the liquids used in the present work were not rigorously purified, the observed increments (Table II) cannot be taken as necessarily representing characteristic properties of the liquids themselves.

(v) *Cracking and Mechanical Properties of Swollen Ebonite.*—Examination of Figs. 1 and 2 shows that the occurrence or absence of cracking does not depend solely on the amount of liquid absorbed. Cracking occurs usually during the initial rapid absorption, as would be expected, as it is evidently due to strains set up by unequal swelling. The observations as a whole, however, are difficult to explain

except on the assumption that different liquids produce specific effects. Generally speaking, sample 3 withstands a greater swelling without cracking than sample 12.

Ebonite becomes much softer when considerably swollen, and the swollen material is highly elastic, as already observed by Ariano (*loc. cit.*). It is relatively brittle, however, as it cannot be bent far without breaking.

3. Influence of Ratio of Rubber to Sulfur and Time of Vulcanization

Particulars of the ebonite samples used for this part of the work are given in Table V. Swelling tests were made at 25° C. with two liquids selected from those previously examined (Section 2 above), namely, benzene, (A. R.), representing the type of liquid comprising the aromatic hydrocarbons and chlorine and sulfur derivatives of hydrocarbons, which are absorbed rapidly and to a relatively great extent, and ethyl acetate (90 to 95 per cent b. p.), representing the type comprising certain polar liquids, which are absorbed slowly and to a relatively small extent.

Curves of swelling against time are shown in Figs. 3 (benzene) and 4 (ethyl acetate). The test-pieces swollen in benzene all cracked, usually at the upper half of the rising part of the swelling curve. At the conclusion of each experiment the test-piece was removed and the residual liquid evaporated to dryness to determine the weight of material that had dissolved.

TABLE V

Sample No.	Mixing	Time of Vulcanization at 155° C. (Hours)	Acetone Extract %	Combined Sulfur %	Vulcanization Coefficient
1	Rubber 65, sulfur 35	3	7.8	28.8	45.4
2		3 ³ / ₄	6.0	30.4	47.8
3		5	5.0	31.4	49.5
4		7	4.8	31.6	49.7
5		10 ¹ / ₂	4.9	31.5	49.5
6	Rubber 68, sulfur 32	3	5.9	27.8	42.0
7		3 ³ / ₄	4.1	29.7	44.9
8		5	3.3	30.8	46.7
9		7	2.9	30.8	46.5
10		10 ¹ / ₂	2.9	30.8	46.5
11	Rubber 72, sulfur 28	3	4.1	25.8	36.8
12		3 ³ / ₄	2.6	27.2	38.7
13		5	2.1	27.8	39.6
14		7	2.0	28.0	40.0
15		10 ¹ / ₂	1.9	28.0	40.1

(i) *Results for Benzene.*—The swelling maximum and increment, deduced from the swelling curves, are shown in Table VI. The extraction of soluble matter by the benzene introduces a small error into the swelling measurement because it reduces the weight of the swollen sample and hence the apparent weight of liquid absorbed. As, however, the amount of extracted matter is known (Table VI), a correction for it can be applied.

In considering the relationship between swelling maximum and vulcanization coefficient, it is preferable to express the swelling as volumes of liquid absorbed by 100 volumes of rubber-sulfur compound, not 100 volumes of total sample, because this contains other substances such as free sulfur and resins. If it is assumed that all the liquid taken up by the sample is absorbed by the rubber-sulfur compound, the amount absorbed per 100 volumes of the latter can be calculated. Figures so obtained, making allowance also for the extraction of soluble matter as explained above, are shown in the last column of Table VI.

With advancing vulcanization, the swelling maximum decreases to a minimum and then increases, and at a given time of vulcanization it is less the higher the sul-

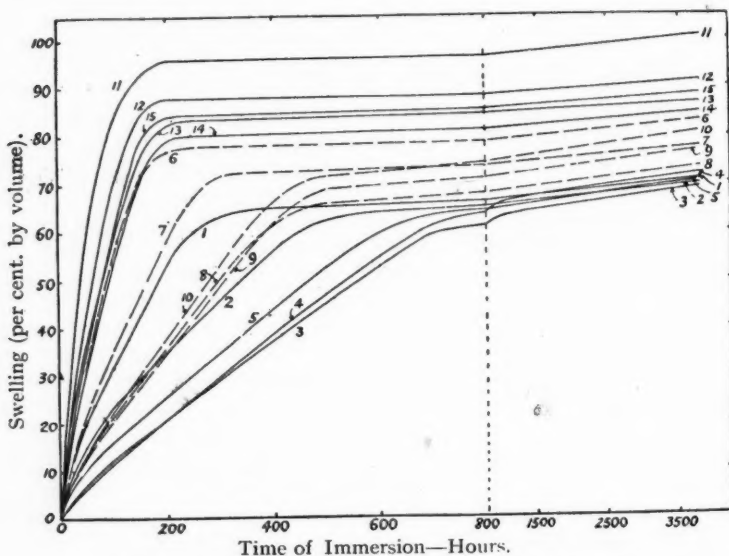


Figure 3—Swelling Curves for Various Ebonites in Benzene
(Numbers on the curves refer to the Ebonite samples)

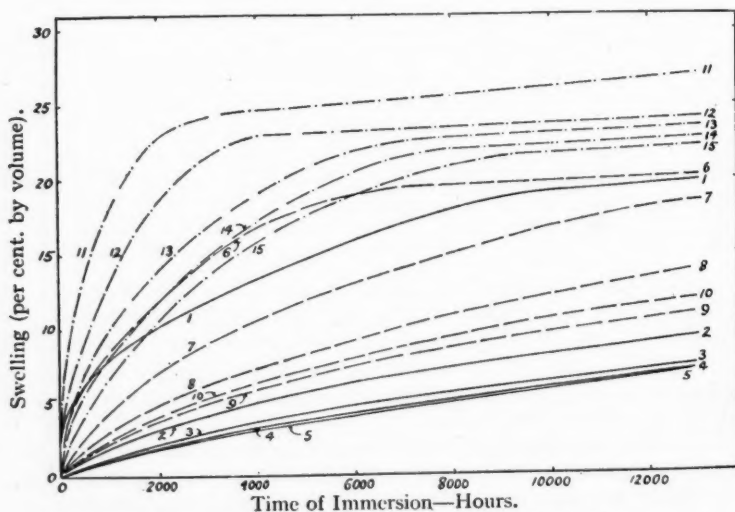


Figure 4—Swelling Curves for Various Ebonites in Ethyl Acetate
(Numbers on the curves refer to the Ebonite samples)

fur content of the mixing. All these effects are similar to those normally observed with soft vulcanized rubber.

TABLE VI
BENZENE

Sample No.	Swelling Maximum (Per Cent by Volume)	Increment	Soluble Matter Extracted (%)	Swelling Maximum of Rubber-Sulfur Compound
1	64.1	0.18	4.4	73.3
2	63.4	0.19	4.1	71.6
3	61.8	0.22	3.6	68.9
4	63.0	0.22	3.3	69.6
5	62.5	0.24	3.1	69.0
6	77.2	0.18	4.3	85.9
7	71.4	0.19	3.1	77.5
8	66.4	0.15	2.2	71.1
9	69.0	0.22	2.0	73.5
10	72.7	0.21	1.9	77.0
11	94.8	0.15	3.7	102.4
12	87.0	0.10	1.6	91.3
13	82.8	0.12	1.4	86.0
14	79.8	0.13	1.6	83.2
15	84.0	0.13	1.6	87.4

Comparison of the swelling maximum of the rubber-sulfur compound with the vulcanization coefficient (Table V) shows that the increase in swelling at the longer cures sets in when combination with sulfur has ceased, and is thus a reversion analogous to that observed with soft rubber. If the samples showing this reversion are excluded, there is, in general, an approximate inverse relationship between vulcanization coefficient and swelling maximum. This obviously cannot be exact, however, as the existence of reversion shows that swelling is affected by other factors besides the vulcanization coefficient.

There are signs that the increment increases with advancing vulcanization in the 65:35 rubber-sulfur and 68:32 rubber-sulfur mixings, and on the average the increment is higher the greater the sulfur content of the mixing. These observations confirm those in Section 2 in showing that the ratio of increment to swelling maximum tends to be higher the more fully the ebonite is vulcanized.

It is obvious from the swelling curves that the rate of absorption of benzene varies considerably among the different ebonites. As the curves do not fit the standard form of swelling curve characteristic of soft vulcanized rubber, the swelling times cannot be calculated by the normal method. It will suffice, however, to consider the times required for the swelling to reach certain given fractions of the swelling maximum (see Table VII).

Absorption is slower the higher the sulfur content of the mixing and the longer the time of vulcanization, except that there is a reversion between 7 and 10.5 hours' cure in the 65:35 rubber-sulfur and 68:32 rubber-sulfur mixings. Although increasing the combined sulfur, whether by prolonging vulcanization or raising the sulfur content of the mixing, thus renders the absorption slower, there is not in general a close relationship between combined sulfur and rate of absorption. Thus, sample 2 has a higher vulcanization coefficient but quicker absorption than sample 8, contrary to the general relationship; samples 6 and 13 show the same effect.

The values of $t^{1/4}/t^{1/2}$ and $t^{3/4}/t^{1/2}$ show how the swelling curves differ from those characteristic of soft vulcanized rubber, for which these ratios are about 0.31 and 2.3, respectively, and also how they vary from one ebonite to another.

Comparison of the figures for soluble matter extracted (Table VI) and acetone extract (Table V) shows that the former probably consists of free sulfur and resins

TABLE VII

BENZENE

$t^{1/4}$, $t^{1/2}$, AND $t^{3/4}$ ARE THE TIMES (HOURS) REQUIRED FOR THE SWELLING TO REACH $1/4$, $1/2$, AND $3/4$, RESPECTIVELY, OF ITS MAXIMUM VALUE. AS MANY OF THE SPECIMENS CRACKED BETWEEN $t^{1/2}$ AND $t^{3/4}$, THE VALUES FOR THE LATTER ARE ONLY APPROXIMATE

Sample No.	$t^{1/4}$	$t^{1/2}$	$t^{3/4}$	$\frac{t^{1/4}}{t^{1/2}}$	$\frac{t^{3/4}}{t^{1/2}}$
1	30	90	165	0.33	1.84
2	53	160	300	0.33	1.87
3	125	310	520	0.40	1.68
4	140	320	515	0.44	1.60
5	110	265	440	0.41	1.66
6	20	57	110	0.35	1.93
7	37	100	180	0.37	1.80
8	61	180	310	0.34	1.72
9	76	200	330	0.38	1.65
10	74	195	320	0.38	1.64
11	14	33	58	0.42	1.76
12	23	49	82	0.47	1.67
13	32	68	110	0.47	1.62
14	31	70	115	0.45	1.64
15	37	80	130	0.46	1.62

only. The rubber-sulfur compound thus appears not to be appreciably dissolved by immersion in benzene at 25° C. for six months.

After removal from the benzene at the end of the experiments the ebonite specimens were dried for 14 days by exposing freely to air at 25° C. Table VIII shows the amount of benzene lost by this drying, expressed as a percentage of the amount in the sample before drying.

TABLE VIII

BENZENE

Sample No.	% Loss	Sample No.	% Loss	Sample No.	% Loss
1	67	6	73	11	79
2	54	7	64	12	..
3	50	8	60	13	..
4	58	9	63	14	72
5	56	10	65	15	73

Drying, like absorption, is slower the higher the sulfur ratio and the longer the time of vulcanization, except where prolonged vulcanization has caused reversion. This is what would be expected, because both absorption and drying are governed by the diffusion constant of the liquid in the ebonite.

Complete drying would apparently take much longer than complete saturation with benzene. Thus, samples 6, 7, and 11-15 are completely saturated after immersion for fourteen days or less, but the saturated samples do not dry nearly so completely in fourteen days. The relative slowness of the drying process, which is found also with ethyl acetate (see below), may be explained by the observation (Section 2 above) that ebonite is much more readily permeable to liquids when swollen than when not swollen. During drying the outside layers are the first to lose their absorbed liquid, thus becoming relatively impermeable and so retarding the escape of the absorbed liquid from the interior.

TABLE IX
ETHYL ACETATE

Sample No.	Swelling Maximum (Per Cent by Volume)	Increment	Soluble Matter Extracted %	Swelling Maximum of Rubber-Sulfur Compound
1	19	2.3	23
2	> 9	0.9
3	> 7	0.8
4	> 7	0.5
5	> 7	0.6
6	19.2	0.005	2.6	23.5
7	18 =	1.1	20 =
8	> 14	0.8
9	> 11	0.6
10	> 12	0.5
11	23.8	0.025	2.4	27.5
12	22.8	0.005	1.3	25.0
13	22.4	0.9	23.9
14	21.7	0.9	23.2
15	21.4	0.9	22.8

(ii) *Results for Ethyl Acetate.*—The swelling curves (Fig. 4) show that samples 6, 11–15, and possibly 1, have reached their swelling maximum. The others would presumably do likewise if the experiments were continued long enough. Tables IX and X give the swelling results in the same way as in Tables VI and VII for benzene.

TABLE X
ETHYL ACETATE

Sample No.	$t_{1/4}$	$t_{1/2}$	$t_{3/4}$	$\frac{t_{1/4}}{t_{1/2}}$	$\frac{t_{3/4}}{t_{1/2}}$
1	80	1700	4800	0.05	2.8
6	300	1250	3000	0.24	2.4
7*	970	3200	6800	0.30	2.1
11	37	380	980	0.10	2.58
12	100	770	1750	0.14	2.27
13	350	1330	3000	0.26	2.25
14	510	1720	3700	0.30	2.15
15	730	2150	4400	0.34	2.05

* Estimated values.

Both the swelling maximum and the rate of absorption decrease with advancing vulcanization, and neither property shows any sign of reversion. It is probable that the swelling maxima of samples 2–5 and 8–10 are not much below 20, and that the relatively small swelling observed even after 13,000 hours (18 months) is due to the extreme slowness with which the swelling approaches its maximum.

The $t_{1/4}/t_{1/2}$ and $t_{3/4}/t_{1/2}$ ratios show that, as in the case of benzene, the swelling curves usually differ in shape from those characteristic of soft rubber.

The swollen specimens were dried, as in the benzene experiments, for periods of 14 and 29 days (see Table XI).

Neglecting samples 2–5 and 8–10, which had not reached maximum absorption, it will be seen that drying, like absorption, is slower the higher the sulfur ratio and the longer the vulcanization, as with benzene. Drying is again slower than absorption, as the fraction of the absorbed liquid that dries off in 14 (or 29) days is smaller than the fraction of the total absorption which occurs in that time.

TABLE XI
 ETHYL ACETATE

Sample No.	% Loss 14 Days	% Loss 29 Days	Sample No.	% Loss 14 Days	% Loss 29 Days	Sample No.	% Loss 14 Days	% Loss 29 Days
1	10	14	6	14	18	11	21	26
2	7.5	10	7	8	12	12	15	20
3	6	10	8	7	9	13	13	18
4	9.5	12	9	7	9	14	12	17
5	9	13	10	7	10	15	10	14

4. Influence of Temperature

It was considered important to investigate the influence of temperature because ebonite shows a profound change in physical properties at temperatures above a critical value ("yield temperature") in the neighborhood of 50° to 80° C. Above the yield temperature it becomes relatively soft and flexible like ordinary, vulcanized rubber. It, therefore, seemed likely that the swelling action of liquids might be considerably greater above than below the yield temperature.

The experiments made so far have been confined to liquids of the paraffin hydrocarbon class, which have practically no swelling action at room temperatures. The yield temperatures of the ebonites examined were as follows (composition and details of vulcanization are given in Table V):

Sample No.	Yield Temperature
1	60° C.
6	50
11	45
12	60

Swelling tests were made with paraffin oil and transformer oil (same samples as in Table II) at 20° and 70° C. As very little swelling occurred after 29 days at 70° C., the temperature was then raised to 100° C. As even 70° C. is well above the yield temperature, any effects due to changes in physical properties above this temperature should be well displayed.

TABLE XII

Liquid	Sample No. and Temp. ¹	1 Day	% Change in Weight after Immersion for: 7 Days	29 Days	32 Days	67 Days
Paraffin oil	1. 20° C.	-0.05	-0.1	-0.1	-0.05
	1. 70-100° C.	+0.05	+0.02	+0.35	+0.6	+0.8
	6. 20° C.	-0.05	-0.1	-0.1	-0.05
	6. 70-100° C.	+0.2	+0.5	+0.9	+1.45	+1.85
	11. 20° C.	-0.05	-0.05	-0.05	0.0
	11. 70-100° C.	+0.95	+2.8	+3.8	+4.25	+4.55
	12. 20° C.	0.0	-0.05	-0.05	0.0
	12. 70-100° C.	+0.45	+1.3	+2.1	+2.9	+3.9
	1. 20° C.	0.0	0.0	0.0	0.0
	1. 70-100° C.	-0.1	-0.15	-0.25	-0.25	-0.25
	6. 20° C.	-0.05	-0.05	-0.1	0.0
	6. 70-100° C.	-0.1	-0.25	-0.25	-0.35	-0.3
Transformer oil	11. 20° C.	0.0	-0.05	-0.1	0.0
	11. 70-100° C.	0.0	-0.2	-0.2	-0.3	-0.15
	12. 20° C.	-0.05	-0.05	-0.15	0.0
	12. 70-100° C.	-0.05	-0.25	-0.25	-0.3	-0.05

¹ In the 70-100° C. experiments the temperature was 70° C. for 29 days and 100° C. after this.

In view of the very small changes in weight observed and the fact that many of these were negative, there is no point in converting the results into change in volume, as is usual. Results are therefore given simply as percentage change in weight (Table XII).

With paraffin there is a measurable absorption of liquid at the higher temperature, and this is less the higher the combined sulfur content, in accordance with previous observations (Section 2 above). The absorption, however, is very small compared with that observed with soft vulcanized rubber even at room temperatures (100 to 300 per cent).

Transformer oil at either temperature produces merely a trifling decrease in weight which is greater at the higher temperature, and is evidently due to removal of soluble substances.

It may therefore be concluded that rubber-sulfur ebonites containing 25.8 per cent or more of combined sulfur are very little affected by prolonged immersion in paraffin or transformer oil at temperatures up to 100° C.

SUMMARY AND CONCLUSIONS

(a) Experiments are described on the swelling of rubber-sulfur ebonites in numerous organic liquids, with special reference to the influence of the nature of the liquid, the ratio of rubber to sulfur and time of cure of the ebonite, and the temperature.

(b) The rubber-sulfur compound constituting ebonite is not appreciably soluble in any of the liquids examined at 34° C. or in aliphatic hydrocarbon liquids at 100° C.

(c) Ebonite may absorb as much as its own volume of some liquids but is quite unaffected by others.

(d) The swelling curve often shows the same features as that for soft vulcanized rubber, but an important difference arises when the absorption is large, because the absorbed liquid progressively increases the diffusion constant and so changes the shape of the curve. For the same reason, also, the swelling capacity of the liquid has a greater influence than its viscosity on the time required to reach maximum absorption.

(e) Increasing the combined sulfur content of the ebonite reduces the amount of liquid that it will absorb and renders the absorption much slower. In making ebonite to withstand the swelling action of organic liquids, therefore, the aim should be to obtain, by using an adequate proportion of sulfur and sufficiently long vulcanization, the highest combined sulfur content consistent with the required mechanical properties; over-vulcanization, however, may be detrimental. It should be noted that slowness of absorption is in itself an important advantage in uses involving only intermittent periods of contact with volatile liquids which can dry out again between these periods.

(f) The extent to which swelling is reduced by increasing the combined sulfur content from the soft rubber stage to the ebonite stage varies greatly with the nature of the swelling liquid. Two important consequences of this are: firstly, with aliphatic hydrocarbon liquids the swelling action practically vanishes when the ebonite stage is reached; and secondly, conclusions regarding the swelling of ebonite cannot be based on data for soft rubber, because the relative swelling effects of various liquids are quite different in the two cases.

(g) The inertness of aliphatic hydrocarbons such as paraffin and transformer oil towards ebonite persists at temperatures up to 100° C., that is, far above the "yield temperature" or softening point of the ebonite.

(h) The time taken to reach maximum absorption is usually much longer with ebonite than with soft rubber, especially if the maximum absorption is small. For this reason short-period immersion tests on pieces of the usual order of size (say $\frac{1}{4}$ in. thick) give no idea of the maximum absorption, and do not even correctly indicate the relative magnitudes of the maxima for different ebonites. The use of much thinner specimens is suggested as a means of hastening the attainment of the maximum.

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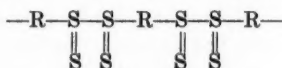
Permeability of Organic Polysulfide Resins to Hydrogen

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A characteristic of balloon and airship fabrics which is of prime importance is that they shall be gas-tight or nearly so. The inherent tendency of hydrogen and of the more costly gas helium to diffuse through thin membranes of rubber provides the incentive for the study of the behavior of a large number of film-forming materials in a search for a more satisfactory material. Considering all of the requirements involved in this application, the permeability of the group of synthetic polymers which are characterized by elastic extensibility has been of particular interest.

The general reaction between organic dihalides with $\text{—CH}_2\text{Cl}$ terminals and inorganic polysulfides yields products which in many cases are characterized as rubber-like. Martin and Patrick^{3,4} suggested that the structure of the polysulfide resins is that of long-chain polymers in which the radicals are connected through disulfide linkages and represented as —R—S—S—R—S—S—R— . According to their hypothesis, any additional sulfur in the material in excess of that required to provide the disulfide linkages is believed to be coordinately linked to the sulfur comprising the disulfide linkages. The structure is represented as



with the added possibility that the coordinately linked sulfur may be in a *trans* rather than a *cis* arrangement. The radical may be derived from ethylene or one of its homologs, or it may be obtained from a reactant containing an ether group, a sulfide group, or an unsaturated group. It is of interest particularly in connection with the present discussion that certain of these products exhibit elasticity both when the amount of sulfur is confined to that representing the disulfide linkages and when the primary molecule contains sulfur in excess of these linkages.

What is often given as the specific example of the formation of this type of plastic is the product obtained when the reactants are dichloroethane and sodium polysulfide. Shortly after the addition of this material to the growing list of synthetic plastics, a compound containing this material was applied to a closely woven fabric by calendering. The weight of coating was 5.2 ounces per square yard (176 grams per square meter). The permeability to hydrogen of this fabric was found to be 0.014 cubic foot per square yard (0.5 liter per square meter) per 24 hours. The low permeability of this material can be appreciated more fully when it is stated that a fabric coated with the same weight of a rubber compound would have a permeability of as much as twenty times this value.

There were, however, several objections to the use of the polyethylene polysulfide product for this purpose. This material cannot be dispersed in suitable solvents and does not therefore adapt itself easily to application in the form of a plurality of thin films to fabric. A somewhat less important objection is its distinctive and unpleasant odor which made it undesirable for use on gas-cell fabric aboard an airship. With the extension of this general reaction to include other organic dihalides

and the production of materials which are capable of being dispersed in solvents to form cements, their utility was greatly enhanced and their laboratory investigation rendered comparatively simple. The odor of these products is, moreover, much less offensive.

Experimental Method

The materials were prepared in a manner similar to the preparation of rubber cements; the resins were masticated on a differential speed mill and the compounding ingredients were added on the mill. The compounds contained 10 parts of zinc oxide and 0.1 to 0.2 part of such accelerators as tetramethylthiuram disulfide and benzothiazyl disulfide. Thin cements were prepared by dispersing the compounds in β -trichloroethane. In the preparation of films unsupported by fabric, the cements were applied to regenerated cellulose sheeting which had not been coated with any moisture-proofing composition.⁵ After being cured in dry heat for 50 minutes at 130° C. (266° F.), the uncoated surface of the regenerated cellulose was moistened with water. The polysulfide films could then be removed without any appreciable deformation. In the preparation of coated fabrics, the cements were applied to closely woven balloon cloth by means of a small spreading machine. The curing conditions were the same as for the unsupported films.

The permeabilities were determined by means of a gas interferometer of the Rayleigh type. The apparatus and conditions of test have been previously described.¹

Permeabilities of Films Unsupported by Fabric

Table I presents the permeabilities to hydrogen obtained with unsupported films of different thicknesses. The organic polysulfide products represent the disulfide and tetrasulfide derivatives obtained from the reaction between 2,2'-dichloroethyl ether and sodium polysulfide. Values obtained with rubber films of approximately corresponding thicknesses are included for comparison.

TABLE I
PERMEABILITIES TO HYDROGEN OF UNSUPPORTED FILMS

	Av. Thickness		Permeability		Specific Permeability
	Cm.	In.	L./Sq. M./ 24 Hr.	Cu. Ft./Sq. Yd./24 Hr.	
Disulfide derivative	0.030	0.012	0.6	0.018	12.5
	0.025	0.010	0.8	0.024	13.8
	0.017	0.007	1.4	0.041	16.2
	0.015	0.006	1.5	0.044	14.6
	0.011	0.004	2.2	0.065	16.8
Tetrasulfide derivative	0.033	0.013	0.2	0.006	4.5
	0.024	0.010	0.4	0.012	6.6
	0.019	0.008	0.6	0.018	7.9
	0.016	0.006	0.8	0.024	8.8
	0.009	0.004	1.2	0.036	7.5
Rubber	0.030	0.012	10.0	0.295	208
	0.025	0.010	14.2	0.419	246
	0.018	0.007	20.0	0.590	250

The results indicated sufficient uniformity to warrant the calculation of what may be called the "specific permeability," or the volume of gas passing through a unit area of a material of unit thickness in unit time. This was calculated by means of the equation:

$$P = Vd/At$$

where P = specific permeability
 V = hydrogen volume, cc.
 d = thickness, cm.
 A = area, sq. cm.
 t = time, min.

The values for the specific permeability of rubber are in close agreement with those obtained by Kayser² and Edwards and Pickering.¹ The values obtained with both the disulfide and tetrasulfide derivatives are much lower than those with corresponding thicknesses of rubber, and those of the tetrasulfide product are consistently lower than those of the disulfide derivative.

Although the specific permeabilities of the disulfide and tetrasulfide derivatives are of the same order of magnitude, they are not constant. This would appear to

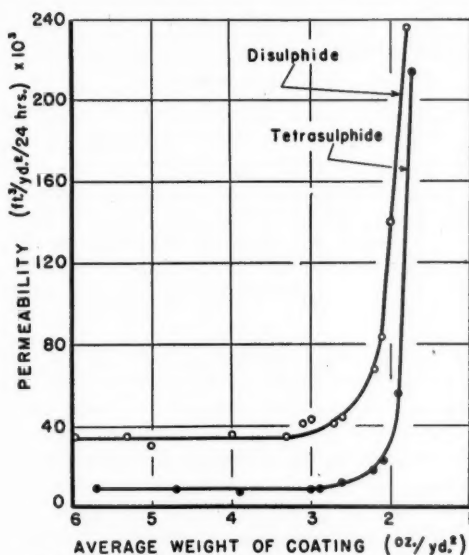


Figure 1—Permeabilities Obtained on a Fabric Coated with Different Weights of Two Polysulfide Resins

indicate that permeability in the case of these materials is not a linear function of the thickness. A possible explanation for this deviation is that the permeabilities were determined with a slight excess of pressure on the hydrogen side of the test specimen (30 mm. of water) which in the case of thin films may have produced a small undeterminable reduction in thickness while under test.

Permeabilities of Coated Fabrics

It was previously observed that the permeability of a given weight of rubber of definite area is greatly decreased when it is spread on a corresponding area of cloth.¹ It has also been noted that the thread count of the cloth exerts an influence.⁶ The permeabilities of fabrics of different thread counts, coated with the same weight of rubber, become lower as the thread count increases. The values given in Fig. 1 represent the permeabilities obtained on a fabric coated with different weights of

the two polysulfide resins which were employed in the determinations of the permeabilities of unsupported films. The cloth employed was that designated as HH balloon cloth, a square-woven cotton fabric with a thread count of 120 in both directions; the average weight of a square yard was 2.05 ounces.

The results indicate the same relative difference in the permeabilities of the two derivatives as was obtained in the examination of the unsupported films.

The effect of the supporting fabric upon the permeability is apparent when comparison is made with the values obtained for unsupported films given in Table I. For example, a film of the tetrasulfide derivative with a thickness of 0.009 cm. (0.004 inch) weighs about 4.6 ounces per square yard. When unsupported by fabric, this film has a permeability of 0.035 cubic foot per square yard per 24 hours. If this same weight of material is applied to fabric, the permeability of the coated fabric will be (according to Fig. 1) about 0.008 cubic foot. Likewise, a film of the disulfide derivative 0.011 cm. (0.004 inch) in thickness weighs about 4.2 ounces per square yard and has a permeability, when unsupported, of 0.064 cubic foot. When applied to fabric, the permeability of the coated fabric is about 0.035 cubic foot.

The specific gravity of the compound containing the disulfide derivative is 1.426 and that containing the tetrasulfide derivative is 1.547. The covering power of these compounds is not, therefore, as high as that of a corresponding compound of rubber, the specific gravity of which would be about 0.995. It is for this reason that, in the case of both derivatives, an abrupt increase in permeability occurs with decrease in weight of coating below about 2.6 ounces. As the weight of material applied becomes less, it becomes increasingly difficult to cover the threads of the cloth uniformly with a continuous film. As the film becomes thinner, it is probable that fibers of the fabric will protrude through the film, thus affording channels for leakage.

That the permeabilities become practically constant within the range shown in Fig. 1 would appear to be explainable on the basis of the difference in the permeabilities of films attached to fabric and those which are unsupported. Within the range shown in Fig. 1, the permeability of the impregnated fabric and the thin film overlying it, represented by a weight of coating of about 2.8 ounces per square yard, is apparently the controlling factor in the behavior of fabrics carrying higher weights of coatings. In accordance with this view the permeability of a coated fabric would be lowered further only when the thickness of the overlying film became sufficiently great as to have a permeability lower than that of the raw fabric plus 2.8 ounces of coating. A fabric was prepared on which the total weight of coating was the equivalent of 15.5 ounces per square yard. The permeability of this fabric proved to be 0.003 cubic foot per square yard per 24 hours, a value considerably lower than those in the practically constant range in Fig. 1. The amount of overlying film in excess of the 2.8 ounces per square yard representing the minimum constant value was 12.7 ounces, which corresponds approximately to a thickness of 0.029 cm. Comparison of the permeability obtained with this fabric with that of an unsupported film of about this same thickness indicates fairly close agreement. The behavior of a resin film overlying a base fabric coated with rubber is also explainable on this basis. The weight of rubber applied to the raw fabric was about 0.6 ounce per square yard. The permeability of a fabric coated with this weight of rubber is so high as to be negligible in its impedance value. The rubberized fabric was coated with 4.6 ounces per square yard of the tetrasulfide derivative. The permeability of the complete fabric was found to be 0.038 cubic foot per square yard per 24 hours, a value which is again in close agreement with that of an unsupported film of a thickness corresponding to this weight.

Effect of Pigmentation

It was to be expected that the addition of pigments to compounds containing polysulfide resins would raise the limits of weights of coatings with which very low permeabilities are obtainable, since the presence of pigments decreases the covering power. However, for a given weight of coating the addition of moderate amounts of carbon black did not produce a pronounced lowering of the permeability. This is indicated in Table II.

TABLE II

EFFECT OF CARBON BLACK UPON PERMEABILITY OF TETRASULFIDE DERIVATIVE

Formulas:					
Tetrasulfide derivative	100	100	100	100	100
Zinc oxide	10	10	10	10	10
Carbon black	15	10	5	2	0
Weight of coating, oz./sq. yd.	3.2	3.4	3.0	3.4	3.4
Permeability, cu. ft./sq. yd./24 hr.	0.029	0.023	0.021	0.012	0.010

Permeability to Helium

Because of the accuracy with which the permeability to hydrogen can be determined, this gas is customarily employed in determining the permeability of balloon fabrics. Since helium is employed in lighter-than-air craft in this country as the lifting gas, it is of interest to note the relation between hydrogen and helium permeabilities of a polysulfide resin. A few measurements made on fabrics coated with different weights of coatings on fabric are as follows:

Helium	Hydrogen Cu. Ft./Sq. Yd./24 Hr.	Ratio, Helium to Hydrogen
0.006	0.009	0.66
0.011	0.017	0.64
0.014	0.023	0.60
0.009	0.013	0.66
		Average 0.64

The average ratio is in close agreement with that found previously for rubber.¹

Mechanism of Permeation

In a report which is largely concerned with the practical application of a material,¹ the nature of the data does not warrant definite conclusions regarding the mechanism of permeation. It is possible that the passage of a gas through a material may be simply filtration through intermolecular spacings or, in highly permeable substances, an actual porosity, or it may take place by a process of adsorption of the gas on the surface followed by diffusion through the material. Under practical conditions, particularly with the heterogeneous compositions widely employed, both mechanisms may function. The behavior of the organic polysulfide resins may perhaps be explainable with either. In these resins the sulfur atoms are enormously large compared to the other constituents of the molecule. They are, in effect, linear polymers of sulfur atoms. From the viewpoint of simple mechanical phenomena, the intermolecular spacings of substances containing such large amounts of sulfur must be small and a high degree of impedance might be anticipated. The lower permeability of the derivative containing the greater amount of sulfur might be attributed to a greater structural density in this substance. On the other hand, these materials would be expected to be inert compared to a material such as rubber and hence would offer much less solvent action towards hydrogen. Concerning the relative behavior of the disulfide and tetrasulfide derivatives, it is to be expected

that, as the ratio of the sulfur atoms to the remainder of the molecule is altered, changes in solubility relations would result which would be reflected in the relative permeabilities of these substances.

Acknowledgment

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Bonding

B. J. Habgood

Many of the technical applications of rubber require that it should be bonded to a variety of other materials. For example, in the automobile and aircraft industry the bonding of rubber to metal is becoming increasingly important, not only for flexible engine mountings, silent blocks, and grummets, but also for floor boards, running boards, and even mudguard protectors.

The bonding of synthetic rubber to natural rubber is also technically important. For example, in the printing industries the superior oil resistance of many of the new synthetic rubbers, compared to natural rubber, makes them of great interest, but the construction of large rollers or blankets composed wholly of such synthetic materials may not be feasible from an economic standpoint. If a suitable bond can be produced between such synthetic rubbers and a natural rubber, then composite articles can be manufactured in which the bulk of the article is comprised of natural rubber, and only a relatively thin layer of the synthetic material is placed round the outside where actual oil and grease resistance is required.

Similar considerations also apply in the case of the tire industry, as certain synthetic rubbers have increased resistance to abrasion and would, therefore, give superior life for a given tread thickness. The use of certain synthetic rubbers for side-walls would also be advantageous, owing to their superiority over natural rubber against flexing and particularly sun-checking.

Bonding is to be considered as a special case of adhesion in which the adhesive force across the interface is greater than the cohesive force of the weaker of the two materials being stuck together. It should not be overlooked that the high strength of rubber reinforced with gas black is probably due both to adhesion and cohesion.

In this paper consideration will be given to the bonding of (1) natural rubber to natural rubber; (2) natural rubber to synthetic rubber; (3) synthetic rubber to synthetic rubber; (4) natural rubber to metals, and (5) synthetic rubbers to metals.

In the study of bonding, an endeavor has been made to assess, as far as possible, the bonds in terms of an actual numerical value. Rubber-to-rubber bonds have been measured on a Schopper machine, using a piece of the bonded material 4 in. long and $\frac{1}{2}$ in. wide. Separation is started by means of a very sharp knife (it is important that this should be very carefully done or erroneous results will be obtained) so that sufficient lengths of separated ends are available to be attached to the dumbbell holders of the Schopper machine. The machine is then started and the bond gradually torn apart. By direct calibration (using weights) the graphical representation of the bond strength can be directly read off as pounds per linear inch.

On the machine used in the tests described in this paper, 1 mm. represents 1 lb. per linear inch except for results below about 20, which are, however, of little interest. These tests were carried out with and without the ratchet in action. More valuable information appears to be obtainable without the ratchet in operation, as in many cases a high initial bond strength is obtained which drops considerably once separation has started. Three main types of curve are obtained (no ratchet) as shown in Figs. 1, 2, and 3.

In some cases the bonding strips have been backed on the sides remote from the bonding surface by stout canvas. A more accurate figure for the actual bond

strength can then be obtained for such samples as the rubber does not stretch, and the width of the bond across which tearing takes place remains constant.

The bond strength of rubber to metal surfaces has been measured by the methods described under A. S. T. M. Designation D 429-35 T (*Standard on Rubber Products*, Oct., 1935, p. 28; Flower and Wening, *Rubber Age* (N. Y.), 35, 282 (1934)).

1. Bonding Rubber to Rubber

The bonding of rubber to rubber is a straightforward job and requires no more than care and cleanliness, provided that adequately balanced cures are employed; for example, similar or identical accelerators should be used at the interface. Cases have actually been known where the use of different stocks has caused ply separation, and the interfacial layer has been found to be so over-cured that the torn surface could be blown off as dust.

Bonding troubles are sometimes caused by the use of liners which have become saturated with a volatile type of accelerator. Mixes off the calender when rolled up and stored before use for a few days sometimes get a slight set on the surface, which then makes plying up a very difficult operation. This type of trouble is

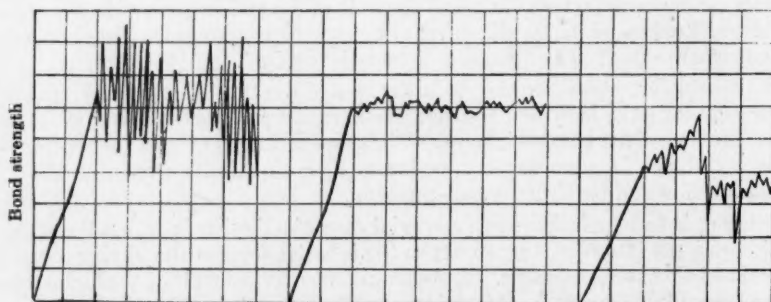


Figure 1—Oscillatory

Figure 2—Steady

Figure 3—Variable

often difficult to trace in the factory, and can lead to a very serious dislocation of output. It is safer, if possible, to keep liners for each different type of accelerated stock.

Sulfur chloride fumes have occasionally given a surface cure which interferes with plying up, but this should not occur in a well-organized factory.

In some cases, for example in the manufacture of rubber-covered rollers, the balancing of curing characteristics is somewhat complicated, as one has to design an ebonite mix to bond on to the metal, then an intermediate mix, and perhaps finally a soft covering mix. In the case of big rollers in particular, highly accelerated stocks are not generally used, owing to the difficulty of obtaining even hardness over the whole roller. Relatively slow accelerators, however, can be used in small quantities, not as a means of speeding up production so much as a means of delicately balancing cures. A critical discussion of the "Technical Problems Connected with Rubber Covering of Iron Rollers" with much data is given in a paper by Gurney and Cameron (*India-Rubber J.*, 71, 554, 601 (1926)).

High wax and stearic acid contents should be avoided in compounds which are required to bond, as blooming of these materials will give trouble due to ply separation after cure. In the case of materials which are designed to withstand sun-checking, this may call for a very delicate balancing of the mixing.

2. Bonding of Natural to Synthetic Rubber

This field is a somewhat complicated one as the methods of obtaining adequate bonding depend on a number of factors. For example, the synthetic rubber itself makes a big difference; some synthetic rubbers bond to natural rubber without difficulty, whereas others bond only when the compounded natural and synthetic rubbers are adequately balanced in composition. In such cases, where the nature of the job makes it impossible to balance the mixes, other methods have to be employed.

At first it was thought that successful bonding depended on similar configuration, and the reason therefore why sodium-butadiene polymers acted as tie-gums between Neoprene and natural rubber was that the complex configuration of such

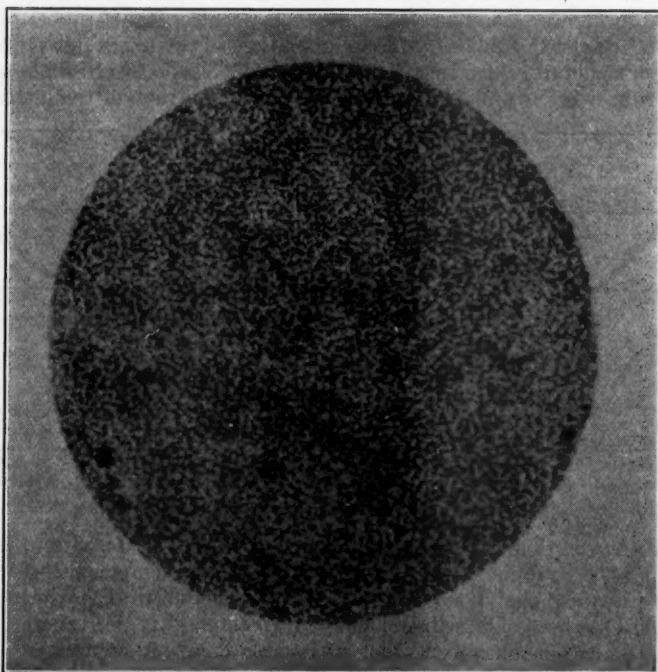


Figure 4

butadiene rubbers was capable of locking into both the *cis*-structure of rubber and the *trans*-structure of Neoprene. This view, however, would not be in agreement with the facts that *trans*-gutta can be successfully bonded to *cis*-rubber but not to *trans*-Neoprene. It is therefore concluded that it is a simple case of intersolubility, and the explanation of the action of butadiene polymers is probably based on their partial intersolubility with both rubber and Neoprene.

The above photograph (Fig. 4) shows that, even after prolonged milling, Neoprene-rubber mixtures are two-phase in structure.

The effect of immiscibility is well shown by the consideration of the variation of tensile strength with the composition of Neoprene-rubber mixtures. The following basic composition was used:

Neoprene	0-100 parts by weight
Natural rubber	100-0 parts by weight
Light calcined magnesia	10 parts by weight
Pine tar	5 parts by weight
Stearic acid	2 parts by weight
Mercaptobenzothiazole	0-5 parts by weight
Sulfur	10-2.5 parts by weight
Zinc oxide	10 parts by weight

It is seen from Fig. 5 that the tensile strength of Neoprene-rubber mixes drops to a minimum figure and then rises again.

Neoprene and rubber gum mixes were made, containing varying ratios of Neoprene and rubber and bonded to Neoprene and to rubber gum mixes. It was found that Neoprene containing 75 per cent or more of rubber will bond to rubber and not to Neoprene, whereas Neoprene containing 50 per cent or less of rubber will bond to Neoprene and not to rubber. Microexaminations of the mixes show them to be two-phase in structure, consisting of a dispersion of Neoprene in rubber or a dispersion of rubber in Neoprene, depending on the composition of the mixture. It

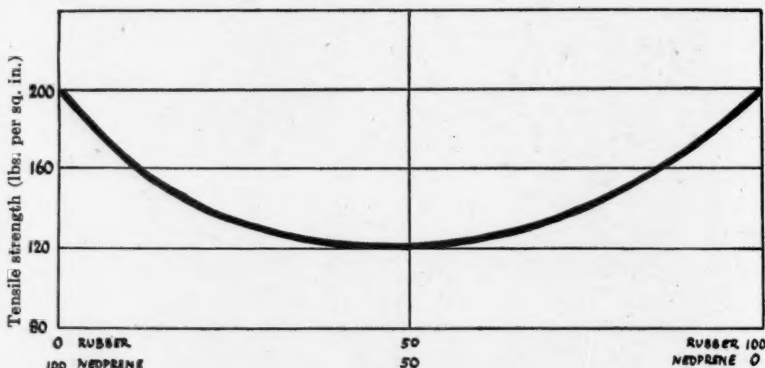


Figure 5

followed, therefore, that if a third component could be introduced into the Neoprene-rubber system to increase the intersolubility of the components, it would be reasonable to expect that bonding could be brought about. Experimental verification of this has been obtained, and many third components are available, the best being chloro derivatives of rubber, which are referred to in some detail later. A. X. F. Plastic, a condensation polymer of ethylene dichloride, benzene, and aluminum chloride; Cardolite, a product made from cashew nut oil, and factice are other products which give good results, the latter being particularly applicable in bonding soft mixes (of Shore hardness 20° to 30°) such as are used for certain types of roller.

Alternatively a vulcanizable product which is intersoluble with both Neoprene and rubber can be used, such, for example, as sodium-butadiene polymers, which are referred to later in more detail.

It has been found that Neoprene can be bonded to natural rubber without any special interfacial treatment, provided that, first of all, the composition of the compounded Neoprene and natural rubber mixes are adequately balanced, and secondly that the operation is carried out with sufficient speed, and that no time is lost between sheeting out the Neoprene and getting it into intimate contact with the rubber mix, or alternatively, the material is kept adequately warm, in which case the time effect does not make itself felt so quickly.

The time effect is well shown by the following series of experiments in which the following mixes were employed:

Neoprene Tread Stock		Natural Rubber Tread Stock	
Neoprene	100	Smoked sheet rubber	100
Light calcined magnesia	10	Zinc oxide	5
Channel black	35	Channel black	40
Wood rosin	5	Mercaptobenzothiazole	0.75
Cottonseed oil	3	Sulfur	3.0
Phenyl- α -naphthylamine	2	Phenyl- α -naphthylamine	1.0
Sulfur	1		
Zinc oxide	10		

The mixes are adequately balanced both as regards rate of cure (optimum 45 min. at 141° C.) and also from the standpoint of volume-loading of filler.

In Table I is given the tearing strength of the bond obtained after varying intervals of time elapsing between the sheeting-out of the Neoprene stock and the bringing-together of the surfaces to be bonded.

TABLE I

Time interval (min.)	0	5	30	120	300
Bond strength (lbs. per in.)	40-50	17	15	15	15

On repetition of this work, keeping the stock at an elevated temperature, namely 70° C., a similar effect (see Table II) is obtained, but to a much smaller extent.

TABLE II

Time interval (min.)	0	5	15	30	120	300
Bond strength (lbs. per in.)	40-50	30	30	30	25	15

The following experiments on the effect of the composition of the materials to be bonded show its importance. The Neoprene mixes were based on the following master batch:

Neoprene	100 parts by weight
Light calcined magnesia	10 parts by weight
Wood rosin	5 parts by weight
Cottonseed oil	5 parts by weight
Phenyl- α -naphthylamine	2 parts by weight
Sulfur	1 parts by weight
Zinc oxide	10 parts by weight
Varying amounts of different fillers being added	

The Neoprene mixes containing the fillers in varying proportions were bonded to rubber compounds containing similar fillers but whose proportion was fixed. The rubber compounds were accelerated with mercaptobenzothiazole. Bonding was in all cases carried out with warm stocks.

The results are given in Table III.

TABLE III

Bond System		Bond Strength
Neoprene plus	Rubber plus	Lbs. per in.
35 channel black	to 40 channel black	40-50
35 soft black	to 40 channel black	20
100 soft black	to 40 channel black	5
150 soft black	to 40 channel black	No adhesion
50 Devolite	to 100 Devolite	10
100 Devolite	to 100 Devolite	20
50 zinc oxide	to 50 zinc oxide	Poor adhesion
100 zinc oxide	to 50 zinc oxide	Poor adhesion

When adequately balanced mixes cannot be used, or when it is not practicable to use Neoprene directly off the rolls or calender or to keep it hot, other methods of bonding have to be employed. Three main methods are available:

- (a) The use of a relatively high concentration of a suitable accelerator at the interface (Habgood and Imperial Chemical Industries, Ltd., British Patent 467,202 (1935)).
 - (b) The use of a tie-gum mix of a butadiene-sodium polymer (Habgood, Morgan, and Imperial Chemical Industries, Ltd., British Patent Appln. No. 36, 119 (1935)).
 - (c) The use of a suitably compounded mixture of Neoprene, natural rubber, and a chloro derivative of natural rubber (Habgood, Morgan, and Imperial Chemical Industries, Ltd., British Patent Appln. No. 8, 170 (1936); 24, 157 (1936)).
- (a) *Bonding Neoprene and Rubber by Means of Accelerator.*—The accelerator can be applied to the interface as a dust. In the following series of experiments the following mixes were employed:

Neoprene Tread Mix		Natural Rubber Mix	
Neoprene	100	Natural rubber	100
Light calcined magnesia	10	Zinc oxide	57.5
Channel black	35	Mercaptobenzothiazole	0.8
Wood rosin	5	Stearic acid	0.3
Cottonseed oil	3	Pine tar	2.5
Phenyl- α -naphthylamine	2	Sulfur	2.5
Sulfur	1		
Zinc oxide	10		

Tests were carried out by curing pieces 4 in. \times 2 in. \times $\frac{1}{8}$ in. in a mold holding twelve samples (cure 45 minutes at 141° C.). The two materials to be bonded were separated by means of a piece of tin for a distance of 1 in. from one end to enable the tearing of the bond to be started easily. The bonded materials were cut into $\frac{1}{2}$ -in. wide strips, and tested in the Schopper machine as described above.

The results obtained are tabulated below:

TABLE IV

Accelerator	Bond Strength (Lbs. per in.)
Zinc diethyldithiocarbamate	36
2,4-Dinitrophenylbenzothiazyl sulfide	50
Tetraethylthiuram disulfide	37
Cadmium pentamethylenedithiocarbamate	60
Lead mercaptobenzothiazole	38
Zinc pentamethylenedithiocarbamate	42
Dinitrophenyl ester of dimethylthiocarbamic acid	35

Similar results are obtained with less heavily loaded Neoprene mixes, but no satisfactory result is obtainable with a tread type of rubber stock containing a large amount of carbon black. Non-reinforcing fillers, for example, blanc fixe, do not interfere.

It is obvious that the application of an accelerator to the interface may not be a very convenient method for some purposes, and good results have been obtained by the use of pastes in which the accelerator is dispersed in vaseline or water. Solutions of tetramethylthiuram disulfide in benzene also give excellent results when wiped over the surfaces to be bonded.

The following series of experiments show the use of a relatively high accelerator content in a tie-gum mix, and are designed to show the effects of concentration of three selected accelerators used in a mix of the following composition:

Rubber	100
Zinc oxide	10
Blanc fixe	75
Stearic acid	1
Sulfur	2

1, 2, 5, and 10 parts of the following accelerators were used per 100 parts of rubber: Zinc diethyldithiocarbamate, tetramethylthiuram disulfide, and dinitrophenylbenzothiazyl sulfide. Stocks to be bonded were of the same composition as those used for the previous accelerator bonds.

Vulcanization and testing of the bonds was carried out in the normal manner, and the results are given in Table V.

TABLE V

Accelerator	Per cent	Bond Strength (Lbs. per in.)
Zinc diethyldithiocarbamate	1	5
Zinc diethyldithiocarbamate	2	48
Zinc diethyldithiocarbamate	5	45
Zinc diethyldithiocarbamate	10	20
Tetraethylthiuram disulfide	1	85
Tetraethylthiuram disulfide	2	45
Tetraethylthiuram disulfide	5	15
2,4 dinitrophenylbenzothiazyl sulfide	1	45
2,4 dinitrophenylbenzothiazyl sulfide	2	56
2,4 dinitrophenylbenzothiazyl sulfide	5	55

The mechanism of the bonding action of accelerators with Neoprene-rubber systems is not at present understood, and although a great deal of experimental work has been done with a view to elucidating the matter, no completely satisfactory theory has yet been evolved. There are, however, some indications that the action may depend on a speeding-up of the rate of cure of the natural rubber component and a slowing down of the rate of cure of the Neoprene component.

Examination of the effect of certain rubber vulcanization accelerators on the viscosity of Neoprene solutions in benzene showed that an increase in viscosity occurred, as will be seen from Table VI. Viscosities were measured at 25° by means of an Ostwald viscometer. The Neoprene solution contained 5 grams of Neoprene per 100 cc. of benzene. 0.3 Gram of accelerator was added to 20 cc. of solution, well shaken, and allowed to stand for twenty-four hours at 25° C. before the viscosity was estimated.

TABLE VI

Accelerator	Times in Secs.	Difference
Control	655
Mercaptobenzothiazole	743.5	88.5
Mercaptobenzothiazole sulfide	716.5	61.5
Tetraethylthiuram disulfide	693.5	38.5
Zinc diethyldithiocarbamate	826.5	171.5
Zinc pentamethylenedithiocarbamate	750	95
Zinc salt of mercaptobenzothiazole	798	143
Lead salt of mercaptobenzothiazole	755	100
Zinc dibutyldithiocarbamate	876	215

The increase in viscosity is the exact opposite of what occurs when accelerators are added to similar solutions of natural rubber, when a decrease in viscosity occurs.

Naunton (*J. Soc. Chem. Ind.*, **44**, 243 (1925)) showed that the vulcanization-promoting properties of organic compounds soluble in benzene could be determined by their influence on the viscosity of a benzene solution of rubber.

It appears possible, therefore, that organic rubber accelerators may act as delaying agents of the vulcanization of Neoprene. The following series of experiments were made to determine the effect of accelerators on the curing of Neoprene.

A standard Neoprene mix of the following composition was made up:

Neoprene	100 parts by weight
Light calcined magnesia	10 parts by weight
Wood rosin	5 parts by weight
Zinc oxide	5 parts by weight

A portion of the mix was retained as a control, and to other portions, 0.5, 1.0, and 5.0 parts of zinc diethyldithiocarbamate (ZDC), butyraldehyde-aniline (BA), mercaptobenzothiazole (MBT) were added, calculated on 100 parts of Neoprene. Tensiles were evaluated by standard method.

TABLE VII

Accelerator	Cure (Min.)	Tensile Strength (Kg. per Sq. Cm.)			Elongation %			Modulus at 600%		
Nil (control)	15	186			1091			52		
	30	190			982			52		
	45	187			965			53		
	60	181			962			52		
	90	180			945			54		
Accelerator %	Cure (Min.)	Tensile Strength (Kg. per Sq. Cm.)			Elongation %			Modulus at 600%		
		0.5%	1.0%	5.0%	0.5%	1.0%	5.0%	0.5%	1.0%	5.0%
ZDC	15	177	170	115	1073	1093	1033	42	43	40
	30	183	175	128	1022	1065	1078	48	43	42
	45	190	168	136	1035	1036	1133	48	44	41
	60	181	168	137	1016	1042	1105	48	44	41
	90	180	179	137	1003	1053	1098	48	45	40
BA	15	135	135	140	1000	974	971	49	54	36
	30	147	178	141	960	1033	878	42	49	43
	45	189	182	137	980	933	824	48	57	50
	60	183	189	133	965	903	810	49	63	50
	90	171	174	130	946	878	796	49	63	53
MBT	15	168	173	90	1043	1143	937
	30	189	182	90	1011	1083	920
	45	176	173	113	1000	1060	1140
	60	184	183	116	1047	1076	1040
	90	178	181	136	1015	1053	1113

It is readily seen from the above tables that the incorporation of relatively large amounts of certain organic accelerators definitely slows down the cure and decreases the modulus and tensile strength. Similar results are obtained with Neoprene mixes containing sulfur.

In view of the above results, much work has been done on the effect of set-up restrainers on bonding, standard methods being employed which will not, therefore, be discussed here.

The set-up of Neoprene can definitely be retarded by incorporation of most acids, and adipic acid appears to be particularly efficacious in this direction, but does not particularly aid bonding. It follows, therefore, that the above experiments do not by any means completely elucidate the mechanism of bonding rubber and Neoprene by means of accelerators; for example, 2,4-dinitrophenylbenzothiazyl sulfide is a relatively slow accelerator and gives excellent bonds, whereas if admixed with diphenylguanidine and so speeded up it does not give such good bonds.

With more accurate information about the molecular weights of natural rubber and Neoprene, it may be found that the action of the accelerator has been to reduce,

by chain-splitting, the molecular weight of the rubber and to increase the molecular weight of the Neoprene, and in this way increase the similarity and hence the bonding of the two substances.

Much work, however, remains to be done before an adequate explanation can be confidently suggested.

(b) *Bonding Neoprene and Rubber by Means of Butadiene Polymers.*—Tread stocks of Neoprene and natural rubber may be bonded by interposing a tie-gum compounded to the following composition:

Sodium-butadiene rubber	100
Channel black	50
Stearic acid	2
Zinc oxide	10
Mercaptobenzothiazole	1
Sulfur	2

and curing together in a press. A bond strength of about 40 lbs. per in. is obtained by this method. Practically no strength is lost after fifteen hours' flexing in the rocker apparatus. This method can also be used with butadiene interpolymer rubbers.

(c) *The Use of Halogen Derivatives of Natural Rubber.*—Halogen and more particularly chloro derivatives of rubber may, after suitable compounding, be used as tie-gum mixes to bond Neoprene and natural rubber, whether either or both are in the form of gum or highly loaded stocks.

Many different chloro derivatives have been examined, including rubber fully and partly reacted with chlorine, hydrogen chloride, hypochlorous acid, alkyl hypochlorites (Farmer and Rubber Producers' Research Association, British Patent 433,082 (1934)), thionyl chloride, sulfuryl chloride, etc.

The best results have been obtained with partly hydrochlorinated derivatives of rubber, which are prepared by passing hydrogen chloride into a solution of milled crepe rubber in benzene until the reaction has reached the desired stage, allowing to stand, and then steam-blowing off the excess hydrogen chloride and solvent. Final traces of hydrogen chloride are removed by kneading with dilute ammonia, washing on a rubber mill, and finally sheeting and drying.

Rubber hydrochlorides vary between soft rubber-like materials to hard horny products, according to whether they contain a low or high proportion of combined chlorine.

The following tie-gum mixes were used to study the bonding of Neoprene and rubber by means of halogen derivatives of rubber. Two types were used, the "ternary mixes" containing Neoprene, natural rubber, and the chloro derivative of rubber, and the "binary mixes" containing Neoprene and chloro derivatives of rubber only. Of course, in each case suitable amounts of the usual accessories for vulcanization were also incorporated into the mix, the terms "binary" and "ternary" referring only to the principal ingredients.

Ternary Mix		Binary Mix	
Neoprene	100	Neoprene	100
Natural rubber	70	Chloro derivative of rubber	100
Chloro derivative of rubber	50	Light calcined magnesia	10
Light calcined magnesia	10	Wood rosin	5
Stearic acid	1	Stearic acid	1
Wood rosin	5	Mercaptobenzothiazole	1.25
Mercaptobenzothiazole	0.75	Sulfur	3
Sulfur	3	Zinc oxide	10
Zinc oxide	10		

Bonding was carried out by placing the thinly sheeted "binary" or "ternary" mixes between Neoprene and rubber (mercaptobenzothiazole) mixes in a mold as described earlier in the paper. The tearing tensile strength of the bond was tested in the standard manner on the Schopper machine.

The results obtained are given in Table VIII.

TABLE VIII

Per Cent Chlorine	Mix	Bond Strength (Lbs. per In.)
6.3	Binary	32.5
7.4	Binary	44.0
7.4	Ternary	45.0
7.5	Binary	45.0
13.0	Binary	48.0
16.8	Binary	45.0
21.5	Binary	30.0
29.5	Binary	27.0

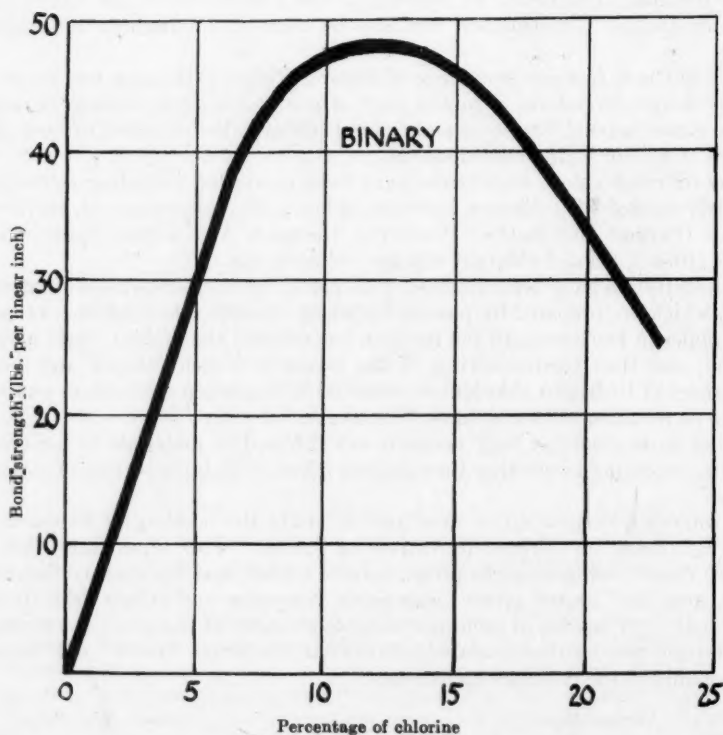


Figure 6

The above graph (Fig. 6) shows the variation of bonding with chlorine content of the rubber hydrochloride when used in a binary mix of the composition given above.

Similar results have also been obtained with rubber which has reacted with varying amounts of chlorine, but the results obtained with such products are, in the

main, not so good as those obtained with the hydrochlorides, and the chlorine content appears to be much more critical, as will be seen from Fig. 7.

The chloro derivatives of rubber can also be reacted with benzene and its homologs in the presence of aluminum chloride, to give resinous products which, when made up into a ternary mix, also give excellent bonds. For example, the product obtained by reacting 40 parts of rubber hydrochloride with 1000 parts of benzene in the presence of 10 parts of anhydrous aluminum chloride when made up into a ternary mix gives an excellent bond, having a tearing tensile of 50 lbs. per linear

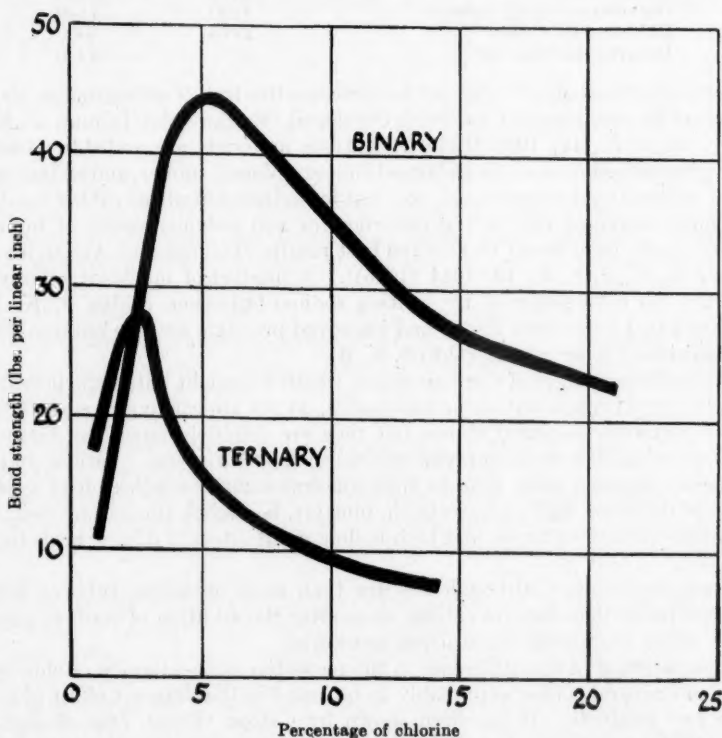


Figure 7

inch, and when tested with canvas backing, a figure of 100 lbs. per linear inch is obtained.

3. The Bonding of Synthetic Rubber to Synthetic Rubber

This is also a complicated field, as the formation of an adequate bond depends on a number of factors; for example, the actual types of synthetic rubber in use and also the manner in which they are compounded both play a big part.

In general it may be stated that the bonding of synthetic rubber to itself or to another synthetic rubber is more difficult than with the natural product, as most synthetic rubbers suffer from lack of tackiness after working on a mill.

The poor adhesion of sodium-butadiene rubber to itself appears to be one of the greatest difficulties that the Russian rubber technologists have encountered, and it is freely admitted in the literature that this has delayed and is delaying the manu-

facture of satisfactory 100 per cent synthetic rubber tires (Evstratov, *J. Rubber Ind., U. S. S. R.*, 10, 797 (1936)).

Great difficulty has also been experienced in the goloshes and soles industries, and softeners such as mineral oil have only partly overcome the trouble (Svëtllov, *J. Rubber Ind., U. S. S. R.*, 10, 333 (1936)).

TABLE IX

	Auto-Adhesion	Tensile Strength
Smoked sheet	3900	3000
Butadiene-sodium rubber	1130	1140
Chloroprene rubber	2775	3000
Interpolymer rubber	1420

Much research is being carried out to overcome this lack of adhesiveness, and new methods of its measurement are being developed (Sharkov and Talmud, *J. Rubber Ind., U. S. S. R.*, 12, 1005 (1935)). Various materials are added to mixings to improve the adhesion, such as reclaimed rubber, mineral rubber, and softeners such as rosin, mineral, and vegetable oil, etc., but for sodium-butadiene rubber the dimers and trimers obtained during the manufacture and polymerization of butadiene ("Eskal") have been found to give the best results (Talmud and Alexandrova, *J. Rubber Ind., U. S. S. R.*, 12, 1014 (1935)). A product of increased adhesiveness (S. K. T.) has been prepared by heating sodium-butadiene rubber S. K. B. at 90° C. for 3 to 4 hours with Eskal, and improved products are also obtained by the mere addition of 5 per cent Eskal to S. K. B.

The butadiene rubbers of German origin, whether straight butadiene polymers or interpolymers with non-butadiene substances, do not appear to give such difficulty as those materials discussed above, but they are definitely much less tacky than either natural rubber or chloroprene rubbers such as Neoprene. Various materials have been suggested from time to time for improving the adhesion of synthetic rubbers of this type, and rosin, rosin oil, pine tar, Kautchol, coumarone resin, creosote, pitches of various types, and high-boiling point esters of dibasic acids have all been used.

Chloroprene rubbers, although less dry than most butadiene rubbers, are still much less tacky than natural rubber, even after the addition of rosin or pine tar, both of which are normal vulcanizing accessories.

The explanation of this difference in the respective auto-adhesion of chloroprene rubber and natural rubber is probably to be found in the different effect of oxygen on the two products. It has been shown by Cotton (*Trans. Inst. Rubber Ind.*, 6, 487 (1931)) and Busse (*Ind. Eng. Chem.*, 24, 140 (1932)) that the so-called permanent breakdown of rubber on the mill is very largely due to oxidation, as milling under similar conditions in an atmosphere of nitrogen gives a different type of breakdown, and the rubber acts more as a true thermoplastic and recovers its nerve on standing.

The thermoplastic polymers of chlorobutadiene, *e. g.*, Neoprene, have a greater resistance to oxidation and, furthermore it is probable that the actual vulcanization of this type of rubber is brought about by traces of oxygen.

It follows therefore that prolonged milling of chloroprene rubbers will not increase tackiness, as traces of oxygen tend to bring about chain-building, *i. e.*, vulcanization, instead of chain-breaking, *i. e.*, mastication, so that too much milling may, by causing incipient set-up, actually give a drier surface to the material, which will make bonding extremely difficult either to itself or to other materials.

The oxygen vulcanization, which occurs at the surface of chloroprene rubbers which are allowed to stand before being piled up, may explain the poor results

which are obtained when it is attempted to freshen such surfaces by application of solvent under conditions which would work well with natural rubber, as vulcanized chloroprene is not soluble in aromatic solvents.

TABLE X

Neoprene	100	100	100	100	
Light calcined magnesia	10	10	10	10	
Wood rosin	5	5	5	5	
Tricresyl phosphate	..	1	3	5	
Zinc oxide	5	5	5	5	
Minutes at 100° C.		Plastic Recovery			
0	22	14	17	13	
10	27	17	18	16	
20	29	20	20	18	
30	46	37	31	29	
45	44	..	46	46	
60	65	51	56	54	
75	71	67	61	55	

However, quite satisfactory building-up can be obtained even with very high loaded stocks, for example, those containing a carbon black loading of 120 volumes or even more, provided that the stock is used fairly soon after it has been sheeted out and is kept warm. Stocks which have been allowed to stand for a considerable time should be resheeted.

By the addition of certain plasticizers, for example tricresyl phosphate, dimethyl phthalate, and similar high-boiling point esters, camphor and similar terpenic ketones (British Patent 457,310, (1936); British Patent 457,311 (1936)), stocks can be obtained which do not harden at the surface so quickly. This is not due to the retarding effect of such plasticizers, as they do not appreciably effect rate of set-up, as is shown by the following experimental data.

The mixes given in Table X were made, and the scorching properties of these mixes were followed by determining the percentage recovery of the material at 70° C. in a parallel-plate plastometer with a load of 1 kg. after varying periods of heating at 100° C.

As would be expected, less difficulty is experienced with softer mixes and much better results are frequently obtained by compounding to a certain hardness by using large amounts of reinforcing filler and large amounts of softener. Such a method has a twofold advantage in that not only is a cheaper mix obtained, but also the larger quantity of softeners present helps bonding considerably.

It is difficult to generalize with regard to the bonding of various synthetic rubbers one to another, but it is fairly safe to say that interpolymers of butadiene with unsaturated esters, ketones or nitriles will not bond or only bond with difficulty to natural rubber or to Neoprene, whereas straight polymers of butadiene and its homologs, such as isoprene and dimethylbutadiene, bond quite easily to chloroprene rubber, to butadiene interpolymers and to natural rubber.

This makes it easy to bond incompatible synthetic rubbers either one to the other or to natural rubber by using a suitably compounded tie-gum mix of a straight polymerized butadiene rubber. The actual manner in which the polymerization is carried out does not appear to matter, provided that no non-butadiene component enters into the polymerization. In general, the best results have been obtained with sodium-butadiene polymers.

4. Bonding of Natural Rubber to Metals

During the past decade much work has been done on the technical bonding of soft rubber to metal, and a great increase in the use of rubber-lined equipment has

taken place in the chemical and related industries, and the automobile and aero-plane industries have recently still further extended the field.

Weber (*Gummi-Ztg.* 18, 255 (1903)) put forward a chemical theory on the bonding of rubber to metal, according to which those metals which most readily formed sulfides when in contact with sulfur should give the best adhesion. According to this theory rubber should bond best to tin, zinc, iron, copper, and aluminum.

Ernaux (*Rev. gén. caoutchouc*, 10, 97 (1933)) has also suggested a chemical theory to explain the bonding of rubber to metal. He observes that a thin layer of sulfide is formed, and suggests that in brass there is sufficient copper to ensure good adhesion, but insufficient to destroy the rubber. Nico, during the discussion of this paper, on the other hand, put forward physico-chemical views, and suggested that during vulcanization the structure of the metal itself changes, becoming more porous, thus promoting the adhesion of the rubber.

Gurney and Cameron (*India-Rubber J.*, 71, 554, 601 (1926)) also incline to the physical explanation of bonding, but further suggest that coppering iron surfaces may cause an increase in oxygen absorption, which may help the formation of an inter-layer of rubber resin between the metal and the hard rubber.

(a) *Use of Ebonite for Bonding.*—The use of hard rubber for bonding has been known for a long time, the first patent being taken out as early as 1865 (Lacolange, French Patent 172,050 (1865)) for rubber-lined acid tank wagons. A little later, Wilding (British Patent 299,288, (1892)) took out a patent for lining pumps with ebonite, and Lacolange repeated his patent for the use of ebonite (Lacolange, French Patent 223,472 (1892)).

A special grade of ebonite known in Germany as eisengummi contains iron oxide as a filler, and gives very good bonds to iron (Khaetzkii, *Electrical Insulating Materials*, 1933, 284).

Some Russian workers have shown that 8.2 per cent of iron oxide gives the maximum bonding effect (Bartenev, Zhurablev, and Lozovskaya, *RUBBER CHEM. AND TECH.*, 9, 605 (1936)). Dixon and Roffey (*J. Soc. Chem. Ind.*, 54, 1104 (1935)) have pointed out the importance of the correlation between the rubber manufacturer and the engineer making the plant.

Good adhesion is obtainable by the use of ebonite, but the method has certain defects. Thus, the brittle nature of ebonite makes its use inadmissible in structures which are subject to continuous vibration, and the difference between the thermal coefficients of expansion of ebonite and iron renders its use precarious where large surfaces are exposed to a rapid temperature cycle such as is frequently met with in a chemical plant. Furthermore, the relatively slow curing characteristics of ebonite make it difficult to prevent overcure of the soft rubber unless accelerated ebonite mixes are used.

(b) *Use of Alloys.*—The earliest patent for the use of alloys was one taken out in Germany (German Patent 170,361 (1904)) using alloys of metals one of which combined with sulfur. The use of alloys containing antimony was patented by Rogstar (English Patent Appln. 2306 (1911)) in this country, and in U. S. A., a year or two later by Daft (U. S. Patents 1,036,576 (1912); 1,057,333 (1913); 1,057,334 (1913); 1,120,795 (1914)), who also claimed alloys of copper and zinc with bismuth and arsenic. The alloys were electro-deposited on the metal, and good adhesion to rubber was obtained.

Rockoff (British Patent 365,755 (1930)) obtained good adhesion by first sand-blasting the metal and then spraying on a suitable alloy containing 60 per cent copper, 40 per cent zinc, and no lead. The brassing method of bonding rubber to metal has been discussed at length by Ernaux (*loc. cit.*). The composition of the brass is critical (69–70 per cent copper and 31–30 per cent zinc) and the thickness of the

brassing and absence of oxidation are as important as a freshly prepared rubber surface. McCortney (*India-Rubber J.*, **87**, 353 (1934)) also gives practical information on this method of bonding, and points out that not only is very close control required on the electro-plating important, but that the adequate cleaning of the metallic surface before plating is equally important. He also stresses the necessity for using the plated metal as soon as possible after plating. Storage under humid conditions is to be avoided, and air-conditioned rooms for building rubber to metal are desirable. It is also pointed out that the composition of the rubber plays an important part in the adhesion, only a small percentage of accelerators being effective, those having a slow set-up during the initial part of the cure being the most satisfactory. Ultra-accelerators are not satisfactory. The actual accelerator used varies with the composition of the brass, as certain accelerators work well with one type of brass, whereas others work better with a brass of an entirely different copper-zinc ratio. Antioxidants must be chosen with care, and softeners are critical, the acidic types of softeners being desirable and alkali types such as soap inadmissible. Pigments do not appear to affect the bonding provided they are inert.

(c) *Use of Cyclorubber.*—During recent years much work has been done on the isomerization of rubber by materials such as sulfuric and sulfonic acids, which are believed to cause cyclization of the rubber molecule to produce thermoplastic substances ranging from hard brittle shellac-like materials to less brittle ones resembling balata and gutta-percha (Fisher, *Ind. Eng. Chem.*, **12**, 1328 (1927)). Solutions of these materials in ordinary rubber solvents were first applied commercially by The B. F. Goodrich Company for bonding rubber to metal by the Vulcalock process.

Since that time many other products have been suggested and patented, for example Clarke, Robinson, and Shepherdson and I. C. I. have proposed to prepare similar materials from latex (British Patent 339,398 (1929)). Reaney (British Patent 449,528 (1934)) has taken out several patents for bonding rubber to metal by use of conversion products of rubber and finds an improvement is obtained by adding clay or aluminum powder to the Thermoprene cement as a stiffener. He has also reacted rubber with phosphorus pentachloride in the presence of aluminum sulfate at 160° C. to give a product which can be used for bonding rubber to metal or as a waterproof lacquer or varnish or as a gum-lac substitute.

It has also been suggested that the surface of the rubber to be bonded be treated with a solution of chromium sesquioxide in sulfuric acid and, after washing, drying, and heating to 148° C. for ten minutes under pressure after application to the metal (French Patent 787,072 (1935)). Twiss, Jones, and Anderson have further proposed the use of a mixture obtained by the action of sulfonic acids upon gutta-percha or balata (British Patent 395,430 (1932)).

The actual strength of solution which is used is very important with Thermoprene cements, and the following figures have been obtained by using benzene solutions of material prepared according to British Patent 339,398 (1929).

The following rubber mix was used:

	Parts by Weight
Latex crepe	100
Zinc oxide	10
Blanc fixe	75
Stearic acid	1
Sulfur	3.0
Diphenylguanidine	0.5

The metal (mild steel) was painted with solutions of the adhesive, two applications being made at right angles, the surface being allowed to dry between each

coat. The rubber was placed in position when the final coat was tacky and cured for 75 minutes at 40 lbs.

Table XI shows the effect of concentration, but it must be pointed out that the optimum concentration naturally varies with the particular rubber isomer employed.

TABLE XI

Strength of solution	3%	5%	10%	12%	15%
Bond strength (lbs. per sq. in.)	330	400	490	300	250

The stearic acid content of the rubber mix to be bonded is important, and should be kept reasonably low as is readily seen from Table XII.

TABLE XII

Per cent stearic acid in rubber mix	1	3	5	10
Bond strength (lbs. per sq. in.)	490	175	145	125

The poor adhesion obtained with high stearic acid contents is probably due to migration of the acid to the interface. Similar results would almost certainly be obtained with paraffin wax.

(d) *Bonding by Means of Cements.*—Self-curing cements, either based upon latex or solutions of rubber in organic solvents, also have a wide application. Such bonding is more troublesome to carry out than Thermoprene cementation, but has the advantage of not softening appreciably at high temperatures.

Latex cements are usually of high solid content and contain a proportion of a protein together with the usual rubber vulcanizing ingredients. The protein is rendered insoluble either by the action of heat, or by the addition of a suitable chemical coagulant as, for example, formaldehyde, or potassium dichromate. Westcott (British Patent 309,168 (1929)) was one of the first to use this type of mix, Kevin (U. S. Patent 1,740,184 (1926)) used albumin formaldehyde, and Carson (British Patent 339,421 (1929)) used blood albumin, together with a tanning agent in this type of cement.

Swindin (British Patent 275,316 (1926)) has used a mixture of Portland cement and latex, which is applied to the surface to be lined with rubber. It is claimed that this Portland cement mixture adheres well to a variety of surfaces, even if they are rusted or corroded, and can even be used as a stopping agent for holes. Uncured sheet rubber suitably compounded is then stuck to this priming coat with rubber solution and is vulcanized by low-pressure steam or hot water (Swindin, *J. Soc. Chem. Ind.*, Proc. Chem. Eng. Group, 14, 169 (1932)).

5. Bonding Synthetic Rubbers to Metals

The brassing method can be used with butadiene rubbers and Neoprene, the adhesion of the former being inferior and the adhesion of the latter superior to natural rubber. It is essential to include a fairly high percentage of sulfur in the polychloroprene mix to obtain good bonding to brass, and the following mix gives an indication of the composition which is recommended.

NEOPRENE MIX FOR BONDING TO BRASS

	Parts by Weight
Neoprene	100
Light calcined magnesia	10
Wood rosin	5
China clay	60
Sulfur	3
Zinc oxide	10

Cure 60 minutes at 141° C. or 20–25 minutes at 60 lbs.

Thermoprene cements do not bond chloroprene polymers to metal very satisfactorily, although good results are obtainable with sodium-butadiene rubbers, and also with butadiene interpolymerized with styrene and acrylonitrile.

Better results have been obtained by the use of Neoprene-ebonite cements such, for example, as the following:

	Parts by Weight
Neoprene	100
Crepe	100
Sulfur	30
Dark factice	5
Diphenylguanidine	2
Magnesia	10
Zinc oxide	10

This mixture is made up with benzene or similar solvent to a suitable consistency, and is then painted on to the metal surface, two applications being made at right angles to each other, the surface being allowed to dry between each coat. The Neoprene is placed in position when the final coat is tacky and is cured for 120 minutes at 153° C.

The actual adhesion obtained by this method is quite satisfactory, but the actual Neoprene-ebonite bonding layer is not very strong and can be torn fairly easily.

For this reason, other methods of bonding chloroprene polymers to rubber have been sought, and excellent results can be obtained by using solutions of chlorinated rubber (Haggood and Imperial Chemical Industries, Ltd., British Patent Appln. 6143 (1937)). For example, a Neoprene mix of the following composition is made up:

	Parts by Weight
Neoprene	100
Light calcined magnesia	10
Wood rosin	5
China clay	75
Zinc oxide	10

A steel plate is first thoroughly cleaned and then painted with a 20 per cent solution of chlorinated rubber in xylene and, when tacky, the Neoprene stock is placed in contact and cured for sixty minutes at 40 lbs. A bond strength of over 400 lbs. per sq. in. is obtained, which is still quite strong at 100° C. The same method can be applied with other metals such as aluminum, lead, cast iron, zinc, and brass, although in the case of zinc and brass better results are obtained by the addition of about 5 per cent of sulfur to the chlorinated rubber cement. It is thought that traces of chlorine compounds are given off at the interface during cure, which aids bonding. No deleterious effect is observable on aging samples bonded by this method. By increasing the solution strength of the chlorinated rubber to 30 per cent, increased tackiness is obtained. The tackiness of the solution can also be improved by the addition of small amounts of Neoprene which, however, should not exceed about 5 per cent, or the strength of the bond will be adversely affected.

Many other chlorinated materials have been examined, including partially chlorinated rubber, chlorinated paraffin waxes, chlorinated naphthalenes, chlorinated fatty acids, such as stearic acid, and chlorinated oils, such as tung and linseed, but in no case is a bond approaching that obtainable with fully chlorinated rubber realized.

Excellent bonds are obtainable with different types of Neoprene mixes, even with those containing very high volume (100 per cent and over) loadings of carbon black by the chlorinated rubber method of bonding.

Aging tests have been carried out both in the Geer oven at 70° C. and at 150° C., and in the oxygen bomb at 70° C. under a pressure of 300 lbs. per sq. in. of oxygen. In the tests, strips of iron were bonded with the Neoprene mix referred to above, and also with a Neoprene tread stock containing 35 parts of channel black on 100 parts of Neoprene, by the standard method. These strips were then bent into the shape of a horseshoe and aged, the bond thus being under tension. The bond was quite unaffected after seven days in the oxygen bomb, after seven days at 70° C. in air, and after two days at 150° C. in air.

6. Use of Chlorinated Rubber for Bonding Natural Rubber to Metal

Although natural rubber cannot be bonded directly to metal by means of chlorinated rubber, it may be bonded to aluminum, for example, by first treating the surface of the aluminum with chlorinated rubber and then laying on a thin layer of Neoprene or painting or spraying a solution. The rubber may be bonded to the Neoprene by any of the methods given earlier in this paper. Perhaps the most suitable method for factory use consists in calendering natural rubber and Neoprene stocks containing an equal volume loading of carbon black, bringing these stocks together, immediately after sheeting out under slight pressure and using this compound sheet as an intermediate layer between the rubber stock to be bonded and the alloprene treated metal surface.

Summary

1. Neoprene and rubber can be bonded directly, provided that:
 - (a) the composition of the two stocks are balanced;
 - (b) the stocks are kept warm;
 - (c) bonding is carried out with the minimum of delay.
2. Neoprene and rubber can be bonded by other methods which give greater latitude of working:
 - (a) by the use of a high concentration of accelerator at the interface;
 - (b) by the use of a tie-gum mix made from butadiene rubber (preferably sodium-polymerized);
 - (c) by the use of mixtures of Neoprene, chloro derivatives of rubber, either alone or admixed with rubber. Partially hydrochlorinated rubber is particularly useful in this direction.
3. Synthetic rubbers can be bonded one to another or to natural rubber either directly or through the medium of sodium-butadiene rubber.
4. The bonding of rubber to metal has been considered and the main methods discussed, including bonding by means of ebonite; alloys, particularly brass; cyclorubbers, Thermoprenes, and cements.
5. The bonding of synthetic rubbers to metals has been examined and a new method of bonding Neoprene to a variety of metals, including iron, steel, aluminum, zinc, and lead, has been worked out, using a solution of chlorinated rubber as bonding agent.
6. By combining the various methods described in this paper, rubber may be bonded to metals such as aluminum without brass plating.

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pH Properties of Colloidal Carbon

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IF ONE part of colloidal carbon pigment¹ is boiled for 15 minutes or more with three to ten parts of distilled water and cooled, the supernatant liquid decanted, and the sludge placed in contact with the glass electrode of a pH electrometer, a reading is obtained which is characteristic of the

TABLE I. pH SUMMARY OF CARBON SLUDGES

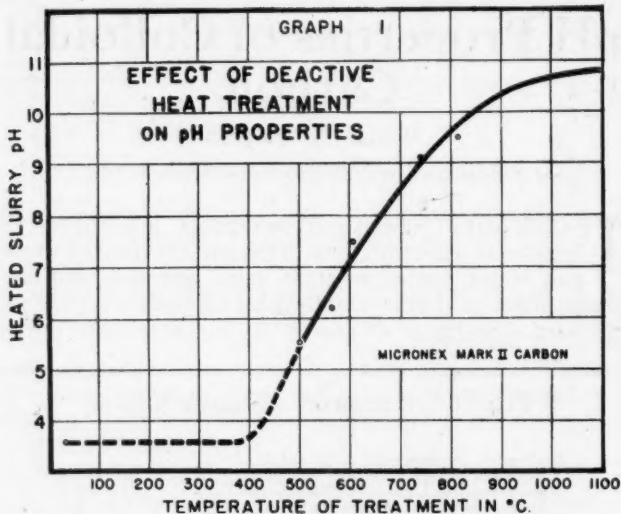
	pH
High-grade impingement carbon blacks:	
Long ink carbon (Peerless)	2.6
Easy-wetting, high-color (Neo-Spectra)	2.8
Highest color (Royal Spectra)	3.1
Medium-color (Superba)	3.2
High-color, general-purpose (Super Spectra)	4.1
Lampblacks:	
High-grade	3.1
Rubber-grade	3.6
Chinese (native) carbon black	4.2
Rubber-grade impingement carbon blacks:	
Slow-vulcanizing (Miconex Mark II)	3.6
Standard vulcanizing (Miconex Standard)	4.1
Fast-vulcanizing (Ultra type)	4.6
Degussa CK 3	5.7
Nonimpingement carbons:	
P-33	8.2
Acetylene black	8.2
Bone black	9.0
Fumonex (or Gastex)	9.3

material. A representative list of the pH values thus obtained is shown in Table I. In this preliminary account some of the factors will be given which influence pH values of particulate carbon, some of the relations between pH and other properties of colloidal carbon, and something of the significance of these pH properties.

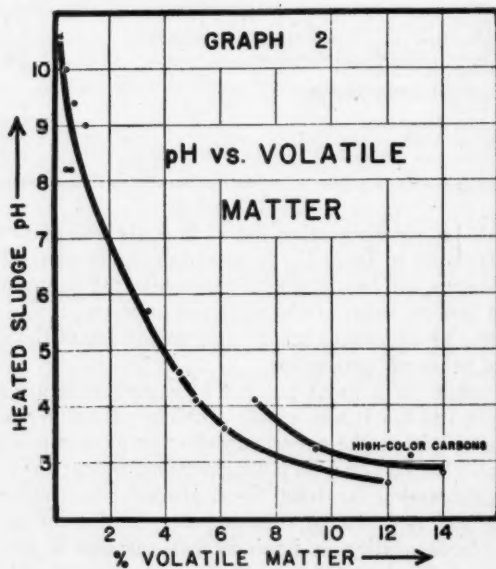
The results of a great number of experiments are shown in Graphs 1 to 4. It was found: (a) The pH value remained unchanged within the experimental error after repeated extraction of the carbon with boiling distilled water; (b) organic solvent extraction (acetone, ethyl alcohol, ethyl ether, and toluene) did not change this property of the carbon; (c) water-soluble acidity in impingement carbons is less than 0.01 per cent calculated as sulfuric acid, part of which has been shown to be sulfur dioxide, but this does not explain their

¹ The family of carbon pigments ranges in particle size from approximately 250 to 5000 Å. Impingement carbons range from about 250 to 700 Å. These are estimated values.

acid properties; (d) carbons produce a greater change in the pH value of neutral salt solutions than they do in distilled



water; and (e) relations have been found between the pH value, the volatile content, and the adsorption index for di-phenylguanidine (D. P. G.).



These results seem to show that the pH change produced by colloidal carbons is an adsorptive phenomenon in which the selective adsorption of the particles of the colloid varies

as some function of the volatile matter content; the higher the volatile matter content, the lower (more acid) is the pH. By heating in the absence of air, a carbon (Micronex Mark II) with an original pH of 3.6 has been given a pH value progressively higher (more alkaline) as the temperature of heating is raised above an apparently critical point. The results of this treatment (each carbon sample was held at the temperature noted for one hour) are shown in Graph 1. In Graph 2 the pH values of various types of carbon are given in relation to their volatile content. Volatile matter is determined as follows: Fill a tared platinum crucible completely with the

TABLE II. COLLOIDAL CARBON PROPERTIES

Grade	pH	D. P. G. Adsorption Index	Per Cent Volatile Matter	Time of Cure in D. P. G. Type Rubber Compound
High-grade, long-ink carbon (Peerless)	2.6	58.4	12.0	...
High-color carbons:				
Easy-wetting, high-color (Neo-Spectra II)	2.8	97.2	14.0	Several hours
Highest color (Royal Spectra)	3.1	96.0	12.8	
Medium-color (Superba)	3.2	77.7	9.4	
High-color (Super Spectra)	4.1	42.5	7.2	
Rubber-grade carbons:				
Fine-particle, slow-curing (Mark II)	3.6	16.0	6.1	50 min.
Standard-curing (Grade A)	4.1	10.1	5.1	30 min.
Fast-curing	4.6	8.4	4.5	25 min.
Degussa CK 3	5.7	5.3	3.4	17 min.
Nonimpingement carbons:				
P-33	8.2	1.8	0.4	15-18 min.
Acetylene	8.2	4.1	0.6	
Fumonex (or Gastex)	9.3	2.5	0.7	
Deactivated rubber carbons:				
HS-421 (1.5 hr. to 1500° F., 0.5 hr. at 1500° F.)	9.0	5.1	1.1	10 min.
HS-355 (2.5 hr. to 2000° F., 0 hr. at 2000° F.)	10.0	4.6	0.4	
HS-335 (2.5 hr. to 2000° F., 3 hr. at 2000° F.)	10.6	4.8	9.2	

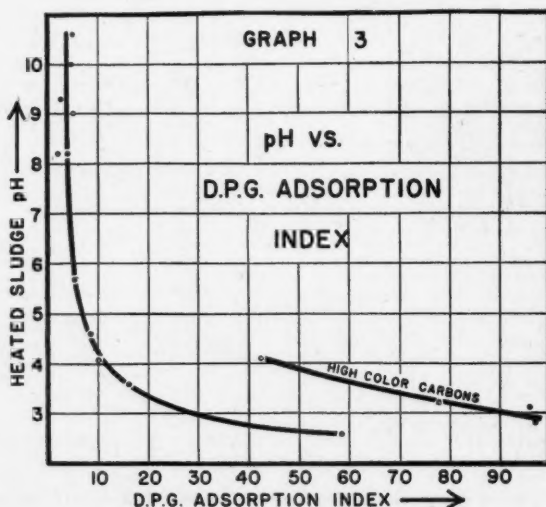
sample. Place the lid tightly in position. Heat for 7 minutes at 950° C. Determine the loss in weight and correct for moisture content.

Graph 3 shows the relation of pH values of the different carbons to their D. P. G. adsorption (X) values. Fifty cubic centimeters of a solution of 2 grams of *c. p.* diphenylguanidine in 1 liter of alcohol are shaken with 1 gram of carbon for 2 hours. After filtering, 25 cc. of the filtrate are titrated with 0.01 *N* hydrochloric acid using a mixture of bromophenol blue and methyl red as indicator. The result is expressed as percentage of D. P. G. removed. Graphs 2 and 3 were both made up from the carbons listed in Table II, which also shows other properties.

The relation between volatile matter and pH seems to offer the key to the situation. Since the volatile content of colloidal carbon is chiefly, if not wholly, made up of oxygen and its compounds with carbon, it seems safe to assume that the carbon-oxygen complex C_xO_y , described by Rhead and

Wheeler (4), may not only account for the original pH values of carbons prepared by different methods but in addition explain the changes in pH observed on deactive heating in the absence of air.

The pH values shown in Table I permit the various families of colloidal carbon to be differentiated. The impingement carbons (including CK 3, according to present information) and the lampblacks give low (acid) pH readings. On the other hand, the finely divided thermal decomposition carbons (P-33) and what may be called the furnace type carbons (Fumonex and Gastex) give high (alkaline) pH values. (Fumonex and Gastex are produced in furnaces involving partial combustion, the heat of which causes separation of



particulate carbon which is, however, not collected by impingement. The true "thermal" carbons are produced without combustion. Both are "born" in a reducing atmosphere.) By subjecting impingement carbons to deactive heat treatment (8), their characteristic pH values can be varied from low to high (acid to alkaline) according to the intensity of the treatment as measured by its time and temperature. The high-color specialty carbons used in inks and paints give low (acid) pH readings, and the rubber carbons fall into an intermediate acid range extending from pH 3.3 to 4.6.

The slow-vulcanizing carbons show lower pH than those which cure rapidly. Most rapid curing of all are the thermal-decomposition and deactivated carbons with the highest pH values. In paints, enamels, and inks the true impingement carbons, which are relatively slow drying, have low pH values. Relatively quick-drying carbons (bone blacks) show high pH.

In Graph 4, pH values and adsorption indices (X) are plotted as variables dependent on volatile content (V). The curves are smoothly drawn from Graphs 2 and 3 and are intended to indicate only broad relations. Four general categories of colloidal carbon may be recognized:

1. Thermal and deactivated carbons, in general, correspond to definitely alkaline reactions ranging from pH 7.5 upwards. The adsorption indices are uniformly below 5, and the volatile contents, in general, are at or below 1 per cent. These carbons include acetylene black, Fumonex, and Gastex, in addition to P-33, and also some forms of graphite, and are markedly quick curing in rubber compounds. This section also includes impingement carbons which have been strongly heat-deactivated to approximately 1.5 per cent volatile, or less. (Thermal carbons of large particle size, such as Thermax and Velvetex, do not appear to have any appreciable pH effect.)

2. The second area may be described as the only blank space in our map. It is populated only by members of the true Ultramiconex series (8) which, owing to their high cost, are not in general use at present. The range in pH is from about 4.75 to 7.5, in volatile content from about 1.5 to 4, and in adsorption of X from about 4 to 7.5. From the manufacturing point of view this range of carbons represents a middle ground between carbons produced under essentially oxidizing conditions and those under essentially reducing conditions.

3. Next comes the range of commercial impingement carbons used in the rubber industry. The pH ranges from 3.3 to approximately 4.6, the volatile content from 4 to 7, and the adsorption index (X) from 8 to 20. This band represents over 85 per cent of all the colloidal carbon now being produced and goes in the main to the reinforcement of tire treads. (Consumption for 1936 is estimated at 363,000,000 pounds.)

4. The specialty carbons are characterized in general by higher volatile content, lower pH, and higher adsorption index. These again are classified according to whether they follow the lower pH and adsorption curves or the upper members which have been designated in the graph as high-color adsorption and high-color pH.

In the former case the curves terminate at Peerless carbon which, while exhibiting no marked difference as regards color or particle size from the rubber group, is distinguished by its low pH, high volatile content, and high adsorption value. In the latter group are included the high-color paint, lacquer, and enamel carbons such as Super Spectra, Superba, Royal Spectra, and Neo-Spectra which may be broadly distinguished by small particle size (about 250 Å., 6) as compared to the rubber and ink grades.

The adsorption curves do not terminate in zero values. This is due to the adsorptive effect associated with specific surface, apart from that due to the combined oxygen. Each particle size will, in general, correspond to a different value for what has been designated X_0 ; the latter value thus becomes an indirect method of estimating particle size. Thus, if the volatile content of Super Spectra is entirely removed by high-temperature deactive treatment, the high-color adsorption curve will cross the ordinate at 34 per cent ($X_0 = 34$).

These differences in particle size must be considered in correlating pH with, for example, the retardation in drying of paints and in the vulcanization of rubber. Thus the retarding effect of a rubber carbon with a volatile content of 7 per cent but an adsorption value of only 20 is not so great as that of Super Spectra with almost the same volatile content but with a much higher adsorption index due to its greater specific surface.

Adsorptive Nature of Colloidal Carbon Acidity

The experimental results, especially those dealing with water-extractable acidity, lead to the conclusion that none of the colloidal carbons should be regarded as a true acid nor any of the thermal or highly deactivated carbons as true bases. In pure water the acid carbons tend to adsorb hydroxyl ions, thereupon taking on a negative charge, the corresponding hydrogen ions are more or less loosely associated or bound. With the alkali-reacting carbons the reverse condition holds. In both cases the outer layer or atmosphere of ions is nevertheless capable of affecting the potential of the glass electrode and is perhaps more significantly capable of influencing the behavior of the carbon in the vulcanization of rubber and the drying of paints.

If, however, these carbons are immersed in a neutral salt solution instead of in distilled water, this powerful selective adsorption results in actual chemical decomposition. With an acid carbon immersed in a sodium chloride solution, the selective adsorption toward alkalies will promote hydrolysis, followed by adsorption of caustic soda and the release of free hydrochloric acid. The extent to which such hydrolysis occurs will depend on the pH value of the carbon and on the strength of the acid.

With basic types the reverse condition will obtain. In general, this behavior of carbon is not different from that of other colloids such as fuller's earth. It is believed, however, that the range (pH 2.6 to 10.6), continuity, and amenability to artificial control of the colloidal carbons here described are unique.

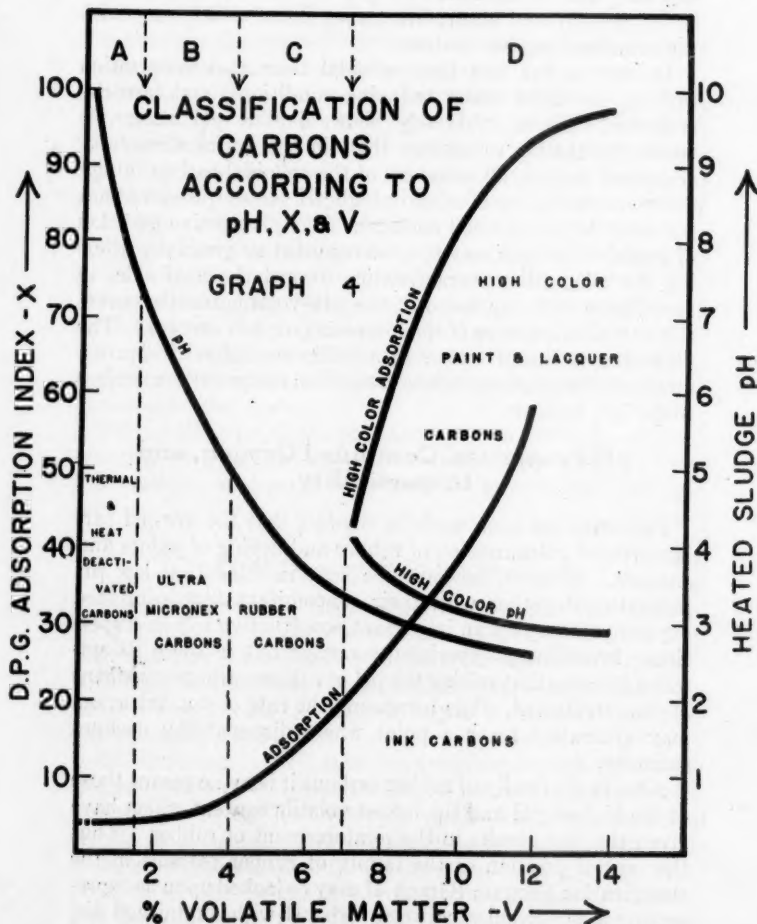
pH Properties and Electrical Charge

The incandescent particles of carbon in the luminous hydrocarbon flame are positively charged and tend to collect on a negatively charged plate or channel (5, 7). When immersed in water these particles, by adsorption of hydroxyl ions, take on a negative charge. The reversal in charge of sugar chars reported by Kruyt (3) when the material had been heated to 1000° C., together with the change in adsorptive activity towards sodium hydroxide solution, may be regarded, in the light of data presented here, as an isolated point in a continuously varying sequence of adsorptive properties, depending

on the surface structure of the material and reflected in its pH values.

pH Properties and Combined Oxygen

The chief ingredient in the volatile matter from carbon black is oxygen in the form of carbon oxides (2). After removal of volatile matter, elementary analysis shows that the



change in composition consists essentially in the elimination of oxygen and, along with it, of carbon (10). The inference is that the bulk of the oxygen content of a carbon can be removed only in the form of carbon monoxide and carbon dioxide, and that it is combined on the surface of the carbon particle in the form of a complex which has been described by Rhead and Wheeler (4) as C_2O_2 .

According to this view the change in pH which occurs after deactive heating and the differences in pH for various types of carbon (Graph 4) may be regarded as due to changes in the amount of C_xO_y complex associated with the pure carbon.

Removal of oxygen decreases the adsorptive activity of carbon toward alkaline substances and instead induces a selective adsorption towards acidic materials (10). This also may now be regarded as a single member of a continuous series, the pH and adsorptive properties of which vary with the combined oxygen content.

In view of the fact that colloidal thermal-decomposition carbons produced under reducing conditions, and heat-deactivated carbons invariably show alkaline pH values, it seems permissible to assume that, in the entire absence of combined oxygen, all members of the colloidal carbon family are characterized by alkaline or high pH values (provided that the particle size is small enough). The progressive addition of combined oxygen may then be regarded as gradually altering the adsorptive characteristics toward the acid side, in accordance with the trend of the pH-volatile matter curve; the latter is a measure of the increasing oxygen content. The flattening of the pH curve at a minimum value of approximately 2.6 suggests complete saturation of the carbon surface with C_xO_y radicals.

pH Properties, Combined Oxygen, and Dispersibility

Reference has been made to the fact that the low-pH carbons retard vulcanization of rubber and drying of paints and enamels. It must, however, be kept in mind that low pH properties, together with their concomitant high combined oxygen values, play an important constructive role in dispersion. Preliminary experiments carried out in these laboratories indicate that raising the pH of rubber carbons by means of heat treatment, while increasing the rate of vulcanization, may ultimately reach a point where dispersibility declines seriously.

Also, in the family of rubber carbons it is by no means those of the highest pH and the lowest volatile content which have given the best results in the reinforcement of rubber. Thus the central position of the family of rubber carbons in the classification diagram (Graph 4) may be looked upon as representing a compromise between high pH with diminished dispersibility on the one hand, and high volatile content involving low pH and excessive retardation of cure, on the other.

pH- C_xO_y and Reinforcement of Rubber

If there is any merit in the hypothesis (6) that the carbon reinforcement of rubber consists essentially in the formation of new physico-chemical complexes between individual macromolecules of the rubber substance and layers of carbon par-

ticles surrounding them, it would seem probable that the C_2O_2 complexes are essential to the bond between carbon and rubber, thus also implying a relation between pH and reinforcement. According to this view and on the basis of a calculation of the oxygen required to form a monomolecular layer on the surface of a carbon particle of diameter 50μ (10), the value for such oxygen content (3 per cent) corresponds to a total volatile content of between 5 and 6 per cent.

This calculation is, of course, subject to various errors, but it invites the theoretical suggestion that the maximum reinforcement of rubber is not likely to occur if the combined oxygen content is depressed much below this level. On the other hand, combined oxygen much higher than this value probably plays no useful role in the development of what may be termed the "reinforcement bond."

The role of fatty acids in the dispersion of carbon in rubber is now recognized as important (1, 6, 9). The higher the C_2O_2 content (with progressively lower pH), the higher appears to be the dosage of fatty acid required to bring out the full reinforcing properties of the carbon (6). It would thus seem that the C_2O_2 contribution to the carbon-rubber bond can reach its highest effectiveness only if the rubber units (macromolecules) are, as it were, activated by the presence of long-chain polar bodies.

On the other hand, the optimum pH (or combined oxygen content) for a rubber carbon is in all likelihood influenced by the available content of fatty acid or its equivalent, in the mixing.

pH- C_2O_2 and Paint Vehicles

The considerations respecting rubber apply with added force to many paint and ink vehicles. This derives from the fact that here mechanical work plays a relatively minor role, with the result that the attainment of complete colloidal dispersion necessitates the highest degree of compatibility between carbon and vehicle.

The heat bodying of linseed oil *in vacuo* leaves the dispersing characteristics of this widely used vehicle in a comparatively low state, whereas heat bodying under oxidizing conditions results in a varnish highly responsive, or activated, to colloidal carbon pigments of the proper chemical structure. The presence in considerable proportions of the oxygen-containing and generally acidic, highly polymerized substances in open-kettle-bodied linseed oils permits and indeed requires a correspondingly higher C_2O_2 , or low pH, in the carbon with which it is ground.

The conclusion is inescapable that ease of dispersion, high "flow" characteristics, freedom from thixotropy, seeding, and other undesirable characteristics depend upon the development of maximum carbon vehicle as opposed to carbon-carbon bond, and that this in turn is governed by the combined oxy-

gen (pH) of the carbon in conjunction with the presence of activating bodies in the vehicle.

The use of very low pH (2.6 to 3.0) carbons in ink and paint may involve retardation in drying, just as those rubber carbons with lower pH values retard vulcanization, so that a compromise may be preferable in this case as well. Often such a compromise need not influence the selection, as in inks where quick surface drying (skinning) is undesirable and in lacquers and some synthetic enamels where drying occurs either by evaporation or by a nonoxidizing mechanism. In such cases the pH of the carbon may be selected with sole regard to dispersion behavior, color, tone, and gloss of the finished product.

Fortunately carbons with a wide range of pH values are already available, so that a selection of the most compatible carbon for any given vehicle can now be made in a systematic, if empirical, manner.

Acknowledgment

The author desires to acknowledge his indebtedness to K. E. Burgess of the Magnetic Pigment Division, Columbian Carbon Company (whose pH studies in the field of iron oxide pigments provided the impetus for this work) for much valuable assistance; to C. W. Sweitzer, Industrial Fellow, Columbian Carbon Company Fellowship, Mellon Institute, who, with the help of W. C. Goodrich and W. C. Eckholm, carried out most of the experimental work; and to E. L. Duhring, director of research, F. H. Levey Ink Division, Columbian Carbon Company, and J. W. Snyder, Binney & Smith Company, for valuable suggestions.

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Some Applications of the Microscope to Rubber Technique

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This paper is not intended to be a review of work done in the rubber industry with the aid of the microscope, but rather a record of some investigations by the authors in this field.

The examination of rubber products usually consists of a chemical examination of the ingredients used, and physical and actual service tests of the finished products. In the course of manufacture one often meets with phenomena which cannot be explained by the results of these examinations. In many of these instances an explanation can be found with the aid of a microscope. Microscopical methods do not seem to hold the place in rubber testing which they merit. This is due partly to the technique required in preparing specimens, and also to the experience required for the proper interpretation of the facts observed.

One must, however, recall the valuable work of Depew and Ruby (*Ind. Eng. Chem.*, 12, 1156 (1920)), Green (*Ind. Eng. Chem.*, 13, 1130 (1921)), Greenquist (*Ind. Eng. Chem.*, 20, 1071 (1928)); 21, 665 (1929)), Steele (*Ind. Eng. Chem.*, Anal. Ed., 2, 421 (1930)), and Ames (*J. Roy. Microscop. Soc.*, 1923, 265).

From microscopical examination of rubber compounds may be deduced: (1) a knowledge of the compounding ingredients; (2) a knowledge of the dispersion of the ingredients in rubber, which will tell a good deal about the quality of the product, *e. g.*, a flocculated ingredient can readily account for many difficulties otherwise inexplicable, and (3) knowledge of the analysis of rubber goods by indicating certain of the ingredients used. It may even be possible to indicate the source of the filler, from the fact that the same filler made according to different processes varies in shape and size.

Almost all compounding ingredients exist today in several commonly used varieties, which might without examination be mutually substituted, but which show noticeable differences on technical testing. It is not always possible to detect chemical differences between two brands of the same product, but it is often easy by microscopical examination to establish differences in the degree of subdivision of two brands, thus providing a physical explanation for observed variations in behavior.

Microscopic slides of common rubber ingredients may be prepared by gently rubbing out under a cover glass a small amount of the powder placed on a slide. Suitable media are glycerine, turpentine, transformer oil, and damar.

A few typical examples of ingredients showing different characteristics under the microscope according to their source or method of manufacture are barium sulfate, whiting, mica, French chalk, magnesium carbonate, magnesia, and zinc oxide.

In a rubber compound, rubber plays the part of a dispersion medium. It is found that the characteristic degree of dispersion of a pigment is being approached during the mixing operation, and has usually been reached by the time the original mixing and subsequent warming-up have been completed. Further working has little or no effect on dispersion. Once this state of dispersion is reached, it re-

mains very stable, even during vulcanization. It should not be imagined that ingredient particles of the same size microscopically will give, in all instances, rubbers of the same physical properties, as one must reckon with coarse structural disturbances which cannot always be discovered by the microscope.

Examination of Rubber Compounds by Reflected Light

This is the best method for preliminary investigation because of the simplicity of the preparation of the specimen. Usually this examination will give an indication of the advisability of an examination by transmitted light.

The method has the advantage of permitting examination of large fields and thus of obtaining a more general view of the surface. It can be employed to obtain information concerning the physical structure of vulcanizates which are built up of individual layers, and it is very useful in the examination of bloom. Irregularities resulting from uneven working or vulcanizing also become evident, often as vaguely bounded colorings, which can only be recognized on large surfaces illuminated by reflected light. Calender grain, extrusion grain, and laminations are best seen by this lighting.

Bloom.—The chief ingredients producing bloom are softeners such as paraffin wax, stearic acid, certain antioxidants, and sulfur, all of which bloom from an uncured compound. In the case of a vulcanized compound, most antioxidants do not bloom to any considerable extent. Some of the antioxidants bloom in the form of needle-shaped crystals which can easily be distinguished from sulfur or wax, and in certain instances from one another.

Stearic acid blooms in the form of patches which are indistinguishable from paraffin wax in appearance, neither having a definite shape. To differentiate them, it is necessary to dissolve the bloom in carbon tetrachloride; then, after evaporation, the addition of alcohol will remove stearic acid and leave paraffin wax undissolved.

A further differentiation of bloom may be made with the use of ultra-violet light from a mercury arc, as substances which bloom usually exhibit a characteristic luminescence. The authors have not had much success with this method with highly compounded mixings, which may contain several fluorescent materials. Other investigators have shown that many antioxidants and accelerators give intense fluorescent colors, but the authors are of the opinion that the presence of more than one fluorescent substance in a compound increases the difficulty of identification considerably, and for positive identification it is necessary to extract the ingredient from the rubber.

Examples of sulfur and antioxidant bloom on a rubber compound are given in Figs. 1 and 2.

Another method of surface examination is to vulcanize the rubber compound to an ebonite and polish the surface. This method is described by Roninger (*Ind. Eng. Chem., Anal. Ed.*, 1933, 251), and was used by Blow and Garner (*Trans. Inst. Rubber Ind.*, 10, 436) for the examination of black dispersions in tread stocks. The sample is cut in the form of a small block (approx. 2 cm. \times 1 cm. \times 1 cm.), cured in molten sulfur (140° C.) for about 18 hrs., and polished on emery paper, slate stone, magnesium oxide paste, and felt pad. It has been used for investigating porosity in casing rubber and similar problems.

Examination by Transmitted Light

Information obtained from a surface examination is limited. Much fuller information concerning the interior of the compound is obtained in an examination

by transmitted light. The opacity of most technical mixings calls for very thin sections for examination by transmitted light.

Several methods of obtaining suitable sections were tried: (a) cutting with a razor, using an unmounted sample or a sample set in paraffin wax or cork, (b) cutting a thin section and stretching, and (c) squeezing a thin section between glass plates.

In the authors' opinion none of these methods is satisfactory, owing to the difficulty of obtaining a section sufficiently thin, and to the distortion produced. The most satisfactory method is to use a microtome. It was obvious from the beginning that the rubber must be hardened, that is, the elasticity must be reduced temporarily in order to cut thin sections. Freezing seemed to be the most feasible method to do this. Liquid air was tried, but dispensed with, owing to the in-

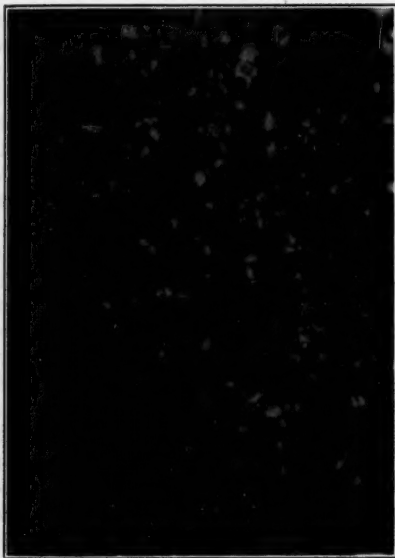


Figure 1—Sulfur Bloom
(Magnification, 35 diameters)

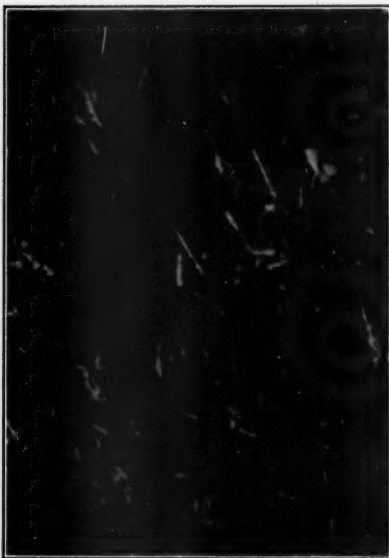


Figure 2—Antioxidant Bloom
(Magnification, 35 diameters)

convenience of manipulation and storage. Carbon dioxide from a cylinder, on the other hand, proved satisfactory from all aspects. This method of producing thin sections for microscopical examination, although simple, calls for a high standard of technique.

Vulcanized Rubber.—For the cutting of sections a heavy sled microtome is used fitted with a freezing stage. The setting of the blade is approx. 45° to the stage and about 10° across the sample to be cut.

A sample (approx. $15 \times 4 \times 3$ mm.) is cut from the rubber to be examined and placed in a small quantity of gum on the center of the stage, the long axis in the direction of the cutting stroke and the 4 mm. side horizontal. The gum should cover the whole of the sample. Carbon dioxide is passed through the stage until the gum solidifies and the sample hardens. The stage is then adjusted until the top of the solidified gum almost touches the blade, and the sample is planed flat,

the coarse adjustment being used before each stroke. Care should be taken during this operation to ensure only a small shaving, thus avoiding damage to the blade and sample. After planing the sample, the stage is pulled well back from the knife, which is moved along through a distance equal to the width of the sample. More carbon dioxide is passed through until the sample is quite hard again, and the sample is moved up to the knife until the surface is just in contact with the edge. One or two preliminary strokes are made, raising the stage by means of the fine adjustment between each stroke until a thin shaving is removed. This is rejected and the knife lubricated with naphtha from a camel hair brush. Without raising the stage, the sample is pushed under the knife with a fairly quick even stroke, avoiding any hesitation as the edge penetrates the rubber. While the stage is still beyond the knife, the section is taken from the edge of the knife by means of the brush and dropped into naphtha. The stage is drawn back, the edge lubricated, and the cycle of operations repeated as many times as required.

Generally about ten sections should be cut, as some will have to be discarded on account of knife markings, etc., which cannot be discerned until the section is laid flat on the slide.

After the second freezing, the operations must be carried out quickly as the expansion of the stage with the rise of temperature is utilized to raise the sample sufficiently between each cut, and this useful rate of expansion appears to occur only over a limited temperature range. By this method the thinnest possible sections (about $\frac{1}{1000}$ mm.) may be cut, and it is, therefore, particularly applicable to tread rubber, which, owing to the high carbon black content, is relatively opaque. In the case of other types of compound, the sample may be raised by the mechanical lift between each stroke.

When sufficient sections are cut, three are selected for examination. These are removed from the naphtha on the point of a pin mounted in a suitable rod, and placed on a microscope slide. The section is now flooded with naphtha and gently turned over with a brush until an end is found. This end is pressed down with the mounted pin, and the section brushed out flat. Until this stage is reached the section must be flooded constantly with naphtha. One end is now dried out with a dry brush; this dry end will be found to adhere to the glass, and by brushing away from this end the rest of the section is dried and laid flat, care being taken to remove wrinkles. The resulting area for vulcanized rubber is about two and one-half times the original.

It is usual to lay three sections on a slide so that extraneous matter, such as dust, will not be confused with material in the rubber. Where any doubt arises, the matter can be settled by reference to the other sections. For the purpose of a direct comparison between two or more samples, it is advisable to cut the sections together. Strips from the samples to be compared are cut and buffed to a thickness of 3 to 4 mm., placed in a 2 mm. mold, and pressed up for five minutes at approximately 50 lbs. per sq. in. steam pressure. This causes the samples to adhere sufficiently for sectioning. The sample is sectioned in the way described above, with the exception that the long axes should be set at an angle to the direction of the stroke of the knife so that knife marks and variation in thickness due to cutting will not coincide with the lines of division between the samples.

Unvulcanized Rubber.—In the preparation of sections of rubber which do not contain sulfur or of rubber which it is undesirable to vulcanize in the ordinary way, some modification of the method described is necessary.

Compounds containing a relatively high proportion of gas black, such as those used for pneumatic treads, may be cut in a similar way to vulcanized rubber. It is not necessary for them to be cut so thinly as the latter, as greater swelling takes

place. The mechanical lift is used, owing to greater difficulty in cutting thin sections. After cutting, the sections must be removed from the naphtha by a section lifter and floated on to the slide. Very delicate handling without brushing is required to flatten these sections, owing to a tendency to breaking. The resulting area is about three and one-half times the original. Carbon blacks of greater particle size than gas black, such as lamp and acetylene black, do not reinforce the rubber sufficiently to prevent it from breaking up when the sections are dropped into naphtha. In such cases cold curing or a light heat cure under slight compression is used, sufficient to give a slight setting-up and cause the least change in the rubber. The samples are then sectioned in the usual way. All types of unvulcanized rubber may, of course, be sectioned after cold curing or setting-up but compounds which do not contain carbon black may be sectioned without any vulcanization by modifying the process. The angle of the blade is reduced to about 30° , and the edge lubricated with water. After planing, the sample is frozen more than in the case of vulcanized rubber. Each section, as it is cut, slides up the blade without curling and is removed directly on to a slide, the surface of which is flooded with water. It is only necessary to dry them off before examination. Sections which are to be preserved for any length of time should be covered with a cover glass and sealed with adhesive binding strip as soon as possible after mounting. The production of satisfactory sections is largely dependent on two factors: firstly the sharpness of the knife, and secondly the temperature of the sample. It is of the utmost importance to have the knife very sharp and free from notches, which will tend to tear and scratch the section rather than cut it cleanly.

In regard to the temperature of the sample, this is rather a matter of experience. If the sample is too hard, the blade will produce a rippled section of thick and thin areas; on the other hand if the sample is too soft, the section will again be patchy, due to the rubber giving during cutting.

General Examination of Compounds

The analysis of rubber compounds by microscopical methods depends largely on comparisons between the unknown and standards of known composition.

A considerable portion of the work lies in routine checking of factory products, and to do this it is generally sufficient to compare the sample to be examined with one of the same compound which is known to be normal. The sample is prepared for sectioning by cutting a strip from the rubber and pressing it against a strip from the standard in a steam press. The composite sample is then sectioned in the way already described.

This method will only give absolute quantitative results when the components of the sample are of the same order as the standard. Where any wide variation is found, it is possible in some cases to give a quantitative measure, depending on the ingredient, the presence of other ingredients and the standards available. In many cases, however, the detection of the variation is in itself sufficient.

In dealing with a sample of unknown composition a preliminary examination will give an indication of the ingredients present. The quantitative estimation of the ingredients may then be made by comparison with known standards.

Carbon Blacks (quantitative estimation).—Carbon blacks in general use are readily distinguished by the color of the light transmitted. Gas black transmits a reddish brown light; acetylene black, gray-brown; lamp black, gray; thermatomic black, blue-gray.

These colors are definite, and the presence of each individual black may be recognized in a mixture of blacks. Any change in color from the standard will indicate such causes as the use of wrong black, mixture of blacks in place of one

black, or wrong proportion in a mixture of blacks. Any change in the intensity of color will indicate the use of a wrong proportion of black. As the standard and unknown are sectioned together, they will be of the same thickness, and any variation of the transmitted light in the unknown will indicate a variation in black content or use of another black.

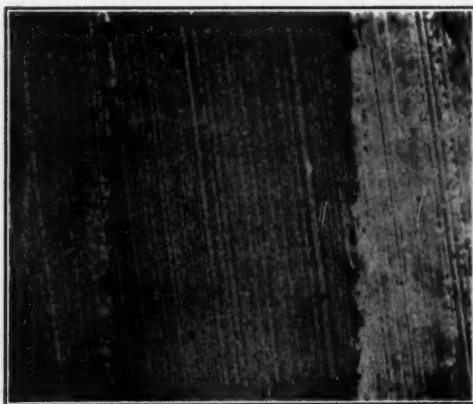


Figure 3
 Lamp Black Acetylene Black Gas Black
 (45 parts) (30 parts) (40 parts)
 (Per 100 rubber)
 (Magnification, 35 diameters)



Figure 4
 Gas Black Lamp + Gas Blacks Lamp Black
 (40 parts) (28 + 12 parts) (40 parts)
 (Per 100 rubber)
 (Magnification, 35 diameters)

Figure 3 shows sections of rubber containing lamp, acetylene, and gas black. It will be at once noticed that there is a very definite difference in appearance, which is very marked when the sections are viewed in their natural colors.

Figure 4 shows sections of rubber containing gas black, a mixture of gas and lamp

blacks, and lamp black; here again there is a definite difference in appearance, which is particularly noticeable in the natural colors of the section.

The authors have not found any other compounding ingredient which affects the color of the light transmitted by sections of a carbon black compound. The statement that different kinds of carbon black can be distinguished from one another by the color of the transmitted light is correct for the blacks in general use, but there are a very few instances in which it needs qualification. The color of the light transmitted appears to depend primarily on the size of the dispersed particles; passing from blue through gray to reddish brown, as the particle size decreases. This same color range is observed in a colloidal dispersion of the different blacks. Thus it is usually impossible by microscopical methods to distinguish between two carbon blacks of similar particle size but of different types. For example, in their investigations the authors found a certain specially prepared black (of natural gas origin) which was indistinguishable from an average sample of acetylene black. A determination of particle size by a method which has been developed in Fort Dunlop Laboratories showed no appreciable difference in the two blacks. Certain physical properties, imparted to the rubber, however, showed marked differences. Carbon blacks, of particle size less than about 0.1μ diameter, are not distinguished by color differences in transmitted light. Thus, sections of rubber compounded with a range of gas blacks of particle size ranging from those usually found in rubber compounding to the still finer varieties found in high grade inks and enamels all give the characteristic reddish brown color. The explanation of this is connected with the phenomenon of light scattering. This occurs, as Lord Rayleigh showed, when light meets in its path particles which are small compared with the wave-length of the light. The intensity of the light scattered by the particles is considered to be directly proportional to the sixth power of the radius of the particle and inversely proportional to the fourth power of the wave-length. This means that the short wave-lengths are scattered much more than the longer ones and the color of the scattered light is blue. The transmitted light with non-absorbing particles (gas black has particles of this type) is, therefore, yellowish red. One should not, therefore, expect differences in particle size within the range which produces scattering to give color differences. This means of course that the color technique cannot be used to distinguish between different gas blacks. In actual practice this would rarely give rise to erroneous conclusions, as the gas blacks used in rubber compounding conform to a certain type and vary little in particle size and other properties. A gas black of an unusual type is readily recognized by its effect on the physical properties of the rubber.

For black estimation, low power is most suitable; a satisfactory combination being the 24 mm. objective with $\times 5$ or $\times 10$ eyepiece giving magnifications of 30 and 60, respectively. For most purposes a 36-watt 12-volt lamp is used as the source of illumination.

Quantitative Estimation of Gas Black.—A range of standard compounds is used having known proportions of black to rubber. For example, one may take a set of standards based on a tread compound, the black and rubber content being 89 per cent of the total mixing weight and the ratios of black to rubber as follows:

	1	2	3	4	5	6
Rubber	66	64	62	60	58	56
Gas black	23	25	27	29	31	33

The sample to be examined is placed between two of them, say (3) and (4); the three are pressed and sectioned together.

The examination will show three things: (1) If gas black is present alone or mixed with some other black. (2) If any other compounding ingredient is present in amounts greater than 5 per cent. When zinc oxide, clay, or whiting is present in greater amounts than 5 per cent, standards will be necessary for the exact estimation of black content. It should be mentioned, however, that there are certain finely prepared whittings and clays which, when present in any quantity, will give misleading figures for black content. The presence and proportion of these may be detected by specific gravity determinations. The same may then be compared with a standard. (3) If the proportion of black lies between those of the standards, or is higher or lower than either.

If the sample is a tread stock, it is probable that gas black is present with only small amounts of other materials. If the proportion is found to be higher than both of the standards the sample must be placed between (4) and (5), or if lower, between (2) and (3), and so on until the correct standards are found. It can then be decided whether the proportion of black of the sample lies between the standards or is similar to one of them. Suppose that it is found to be the same as (4), then it may be concluded that the sample has a proportion of black to rubber of 29 to 60 or 48.3 to 100.

In each of these standards, the black and rubber content is 89 parts by weight, and the remaining 11 parts are made up of sulfur, accelerator, antioxidant, zinc oxide, softeners, etc., in proportions which may be assumed to be generally used in tread compounds, and the total of which will vary very little. By making this assumption, it is possible to give the black content as a percentage of the mixing weight, that is, 29 per cent. It may be that the sample contains reclaim or other material, say 10 per cent, which is recognized and estimated, and that the proportion of black to rubber is the same. The compound may then be reconstructed:

Rubber and black	79 parts
Reclaim	10 parts
Sulfur, etc.	11 parts

The rubber and black are divided in the proportion of 53.3 rubber to 25.7 black.

The accuracy of all black estimations will be affected to some extent by agglomeration, which will affect the amount of dispersed black. The work done so far indicates that variation in cure is capable of causing some change in opacity in tread-rubber sections, but the authors have not yet determined the exact relationship.

Figure 5 shows a composite section of rubber containing 35, 39, and 43.5 parts of gas black to 100 parts of rubber. The difference in the intensity of the light transmitted is very marked.

Dispersion of Blacks.—Individual particles of smaller diameter than those of lamp black and similar relatively coarse blacks cannot be resolved even at the highest magnifications. In the case of channel gas blacks used in rubber compounding, the particles are so small (considerably less than 0.1μ in average diameter) that appreciable agglomerates might be present and not be perceived. A quantitative measure of the ultimate dispersion does not, therefore, appear to be possible by ordinary microscopical methods.

The proportion of agglomerated black, disregarding the smaller aggregates which cannot be measured, may be estimated approximately in a thin section by transmitted light. If the dispersion is very poor the color intensity will be reduced, but within the limits usually encountered in properly mixed stocks, the intensity differences are too small to be of practical value in differentiating between them. A better method is to measure the actual area of agglomerated black in the section.

It is found convenient to use 16 mm. objective in conjunction with a $\times 10$ eyepiece, and the area is estimated by means of the squared eyepiece micrometer which is placed on the diaphragm of the eyepiece at the focal point of the eye lens. The total area of agglomerates in one field is measured in units of one square. The field is selected by inspection as being an average one, and representative of the whole section. Several fields are measured, and the average taken if the amount of agglomeration is small. An allowance has to be made for the swelling of the rubber, and in this respect it has been found that for pneumatic tread compounds in general



Figure 5—Effect of 35, 39, 43 $\frac{1}{2}$ parts of gas black (per 100 rubber)
(Magnification, 35 diameters)



Figure 6—Reclaim in Cycle Tread
(Magnification, 35 diameters)

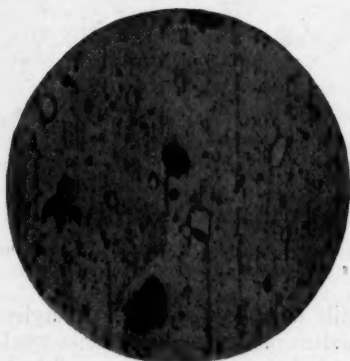


Figure 7—Reclaim in Motor Casing
(Magnification, 35 diameters)



Figure 8—Reclaim in Motor Tread
(Magnification, 35 diameters)

the final area of section after swelling and brushing is of the order of 2.5 times the original.

Although, on account of the assumptions which have to be made, the method is not quantitatively accurate, it gives results which can be repeated, and affords a means of distinguishing quite small differences between the degree of dispersion in different samples.

Carbon Blacks Other than Gas Black.—The method employed is exactly as for gas black. The presence of any ingredient other than black of the same particle size

will give misleading results in the estimation of black. The presence of these ingredients may be checked by specific gravity methods, and the samples then compared with a standard. Such ingredients are zinc oxide and some specially prepared whittings.

Mixtures of Blacks.—The more common mixtures, such as those of gas and acetylene blacks and gas and lamp blacks, are readily recognized, and the total black and proportions of the two blacks can be estimated by the use of suitable standards. But with compounds of an unknown type, the same difficulties as noted before will arise, and the same remarks will apply.

It should, however, be noted that, as the color given by acetylene black is intermediate between those given by lamp and gas blacks, a mixture of the two latter

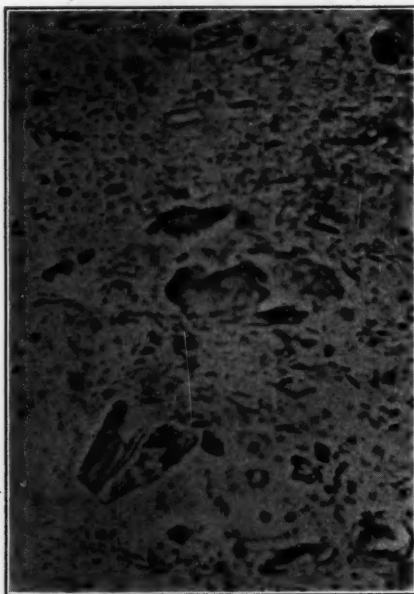


Figure 9—China Clay in Rubber Compound
(Magnification, 350 diameters)

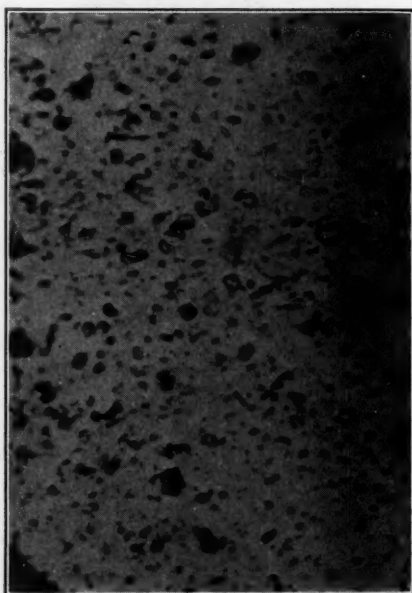


Figure 10—Whiting in Rubber Compound
(Magnification, 350 diameters)

blacks in a certain proportion will not be readily distinguishable from acetylene black. In such a case, which would be rare, a mixture of lamp and gas blacks would show fewer particles (because those in the gas black fraction are too small to be visible) than acetylene black, and on the average the particles would appear larger. A mixture of lamp and gas blacks would, moreover, be distinguishable from acetylene black in the physical properties imparted to the rubber.

Zinc Oxide.—When not in the presence of carbon black or other pigments, zinc oxide imparts to the transmitted light a pale brown color which varies in intensity with the amount of zinc oxide present. It should be noted that different methods of manufacture of zinc oxide give different tints, and the source of the zinc oxide may be sometimes detected. At a magnification of 420 (4.2 mm. objective and $\times 10$ eyepiece) the particles are clearly defined and may be measured if necessary.

Quantitative Estimation of Zinc Oxide.—When zinc oxide is used alone, as in tire casing compounds, it is estimated by direct comparison with known standards.

In the presence of other ingredients it is difficult to estimate, and the accuracy of the determination will depend on the nature of the other ingredients and the amounts present. When the normal method cannot be employed, a rough estimate can be made by consideration of the number of particles in a given area compared with a standard.

Reclaim and Crumb Rubbers.—Reclaim appears in the form of clearly defined patches with characteristic straight sides. Whole cover reclaim, which is met most frequently in tread rubber, will be detected by brown patches slightly darker than the surrounding rubber and by lighter patches than the surrounding rubber, which will be fewer than the brown. These patches are formed from the tread and casing rubbers used in the manufacture of the reclaim. The appearance of the light patches is likely to vary considerably; for example, reclaims from a cover with a high zinc oxide casing will show comparatively opaque patches, whereas those from a low zinc oxide casing will be comparatively transparent.

In other types of rubber compounds containing less carbon black than treads, the brown patches appear much darker and the light patches are less clearly defined.

Other types of reclaim are occasionally found, their color depending on the materials from which the reclaim is manufactured. All reclaims tend to cause porosity in the rubber, and are accompanied by small transparent patches which are characteristic. Crumbs and waste rubbers have a somewhat similar appearance to reclaim, but the patches vary much in shape, are usually more opaque, and appear in greater profusion. They do not tend to cause the same degree of porosity as reclaim, and transparent patches are absent.

Figures 6, 7, and 8 show the presence of whole cover reclaim in cycle tread, motor casing, and tread compounds. In these photographs the presence of the dark and light patches is easily detected.

Quantitative Estimation of Reclaim and Crumb Rubbers.—Estimation is made by comparison with standards, but not directly as in the case of carbon blacks. A preliminary scanning of the section with a 16 mm. objective and $\times 10$ eyepiece gives details of the distribution and size of reclaim, the degree of porosity, and the distribution of transparent patches.

This examination leads to a standard slide which corresponds with the sample under test.

When the reclaim content is low, it is necessary to examine more than one section to gain a true idea of the distribution. The reclaim standards should of course be of a type similar to the sample. The authors are unaware of any chemical analysis which will indicate with any accuracy the amount of reclaim present in a compound.

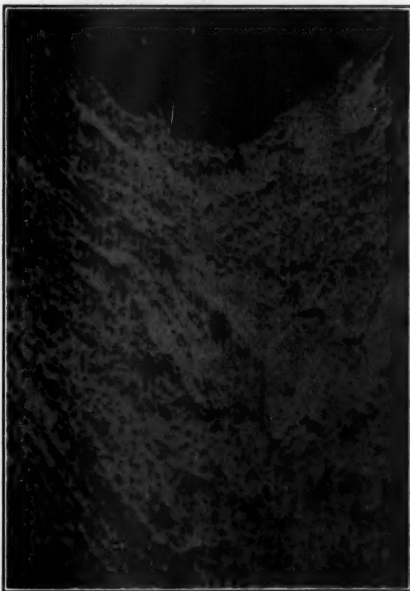


Figure 11—Bad Distribution of Carbon Black in Tire Tread Stock
(Magnification, 15 diameters)

Dark Substitute (Factice).—This material, which is found mostly in mixings used for extrusion such as cycle tubes, tubing, etc., appears as pale brown translucent patches.

China Clay.—This is identified by the plates of mica and by the porosity imparted to rubber. The plates will be often found adhering to the edge of the pores.

Figure 9 shows the plates of mica and the porosity imparted to a rubber mix by the presence of china clay in the compound.

Whiting (ground).—Whiting is indicated by the presence of small shell forms,

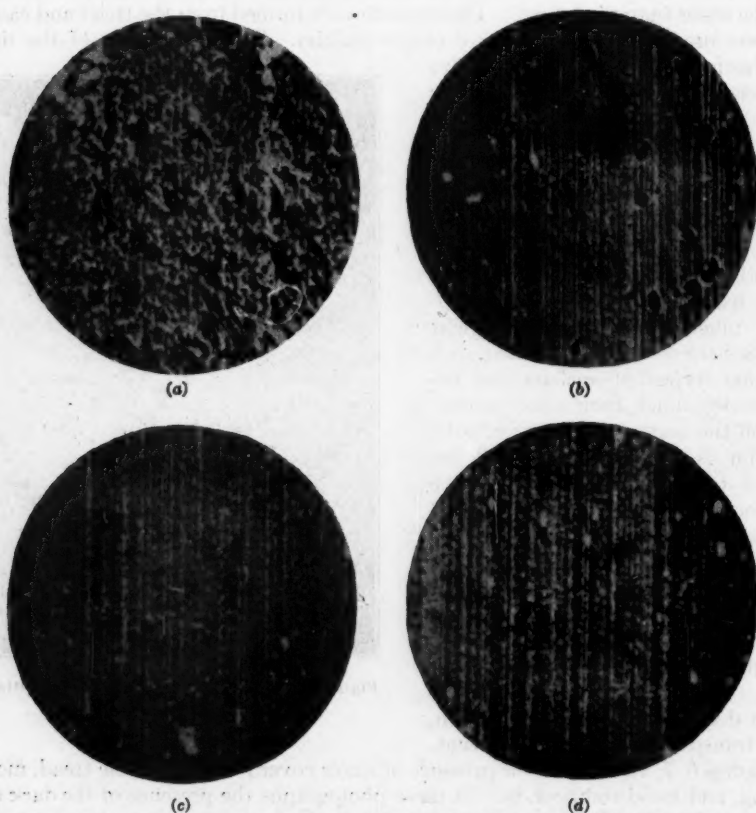


Figure 12—Dispersion of Carbon Black during the Manufacture of a Tire Tread

(a) After first mixing

(b) After second mixing

(c) After warming-up

(d) Finished tread

(Magnification, 55 diameters)

and Fig. 10 shows the small shell formations due to the presence of whiting in a rubber compound.

Magnesium Carbonate.—The particles are acicular but difficult to see, owing to the fact that the refractive index is similar to that of rubber and that during the mixing operation the particles are broken up.

Stearic Acid.—Stearic acid combines with zinc oxide during vulcanization when both are present in the stock, and is seen when the rubber has been allowed to cool fairly slowly and without subsequent heat treatment.

Normally, it appears as circular translucent patches which have a dark outline and are similar to, but larger than, zinc oxide particles. The size and form of these patches vary with the rate of cooling of the rubber after vulcanization, and under special conditions take a flowerlike form.

Quantitative Estimation of Stearic Acid.—Stearic acid may be estimated by direct comparison with standards of known stearic content. The sample is placed in a water bath at 100° C. After about 5 minutes it is allowed to cool slowly in water to room temperature. The stearic acid appears in the form of large flowerlike patches which can be observed easily. The amount of stearic acid is proportional to the number of patches on the section, which is compared with the standard.

Colored Compounding Ingredients.—Such materials as iron oxides, antimony sulfides, and other colored ingredients are difficult to identify, particularly if present with other ingredients.

Photomicrography

A camera of the type which fits directly on to the tube of the microscope is quite satisfactory. The method of taking the photographs has no special features; the difficulties lie rather in preparing and illuminating the object than in the actual photography. The work with reflected light has always been carried out at low magnifications.

The chief difficulty when photographing by transmitted light is the lack of contrast between the various features in the compounded rubber, particularly in rubbers such as pneumatic treads containing high proportions of carbon black. Halation also is troublesome, due to the very intense beam of light which must often be used, combined with the fact that all these sections of rubber cut on the microtome exhibit porosity to a greater or lesser extent. These two difficulties can be overcome largely by the use of slow fine-grained plates which are backed with a light absorbing dye. Further improvement can be effected by the use of glazed printing paper capable of intensifying contrast.

There are numerous instances in general rubber works practice in which the microscope gives valuable aid, and information on processing such as cannot easily be obtained by other methods. Among these may be mentioned (1) agglomeration, uneven dispersions of powders during mixing; (2) comparison of mixing methods; (3) effect of softeners on dispersion; (4) impregnation of cord, and (5) flow of rubber in cord plies during molding. Thus Fig. 11 illustrates an example of bad distribution of carbon black in a tread compound.

Figure 12 illustrates the improvement in the dispersion of carbon black through the various stages of manufacture of a tire tread.

In conclusion, the authors wish to express their thanks to the Dunlop Rubber Co., Ltd., for permission to publish the information embodied in this paper, to A. V. Howson and particularly to B. J. A. Martin for much of the work described herein.

Rapid Detection of Accelerators

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Where doubt exists rubber technologists may at times require a prompt answer as to whether accelerators are present in a rubber compound. It was necessary therefore to develop specific reactions and methods of procedure which make it possible to determine each individual accelerator in the presence of other accelerators.

The procedures developed by us for the detection of accelerators in uncured rubber compounds and for mixed accelerators are extremely simple, and require not more than 10-15 minutes for completion of a test. By these methods a technologist can obtain a quick answer, and thus prevent possible spoilage and rejection of finished rubber goods. The additional advantage of these methods is that each individual accelerator can be detected in any combination of accelerators present in the rubber compound. Qualitative identification is performed almost exclusively in aqueous extracts, and is based on the differing solubilities of accelerators in water.

The tests, described here in detail, were confirmed by tests of all rubber mixes used at the Yaroslav Rubber and Asbestos Works. These mixes contain the accelerators most commonly used in the rubber industry, such as diphenylguanidine, mercaptobenzothiazole, tetramethylthiuram disulfide, K-1 (a condensation product of aniline 2 mols and acetaldehyde 3 mols), and A-19 (formaldehydeacetaldehydeaniline).

DESCRIPTION OF THE REACTIONS

I. Color Reactions with Cobalt Oleate Solution in Benzene

(a) *Benzene Extract of Accelerators.*—A sample of 2-3 grams of the accelerator under investigation is shaken with 10-15 cc. of benzene for 2-3 minutes. The filtrate is then treated dropwise with a benzene solution of cobalt oleate until the solution becomes colored. Under these conditions, diphenylguanidine gives a violet color and mercaptobenzothiazole an emerald green color. Tetramethylthiuram disulfide in benzene solution gives a color reaction only after a prolonged standing.

With commercial mercaptobenzothiazole the green color reaction is masked by contamination with resinous products. In this case, the determination is made in aqueous solution.

(b) *Aqueous Extract of Accelerators.*—A sample of 5 grams of an accelerator in 15-20 cc. of water is boiled for at least 5-7 minutes. To 3-4 cc. of the cold filtrate is added 0.5 cc. of a benzene solution of cobalt oleate, and the mixture is shaken vigorously. Colored rings, characteristic of each accelerator, appear after a short period of settling. Diphenylguanidine gives a violet ring, mercaptobenzothiazole an emerald green ring, and tetramethylthiuram disulfide a deep green to olive colored ring, depending on the purity of the product. Tetramethylthiuram disulfide can be detected only by this reaction. The color of even insignificant admixtures of tetramethylthiuram disulfide predominates over the colors of other accelerators.

(c) *Mixture of Aqueous Extract of Accelerators with Benzene (color reaction of diphenylguanidine and mercaptobenzothiazole).*—To the filtered aqueous extract, ob-

tained as described under (b), 1–1.5 cc. of pure benzene is added. After shaking and settling, the benzene layer is carefully treated drop by drop with a benzene solution of cobalt oleate until the color appears, and the mixture is vigorously shaken again. This is necessary, because in the presence of other accelerators in the sample the original color reaction may change after additional shaking. Thus, for example, in a mixture of diphenylguanidine and tetramethylthiuram disulfide, a benzene extract of the aqueous solution gives a violet color before shaking. After shaking, the violet color disappears and a turbid green color appears, indicating the presence of tetramethylthiuram disulfide.

Under the conditions of this variation of procedure, *i. e.*, in the two-phase medium (benzene and water), tetramethylthiuram disulfide masks the color reactions of diphenylguanidine and mercaptobenzothiazole.

II. The Reaction for Diphenylguanidine with Picric Acid

(a) *Aqueous Extract.*—To the filtrate of the aqueous extract, obtained by the method described above (I (b)), a 1 per cent solution of picric acid is added until a yellow flocculent precipitate of the picrate of diphenylguanidine is formed.

(b) *Extract of Diphenylguanidine with Hydrochloric Acid.*—Approximately 3 grams of the accelerator are boiled with 15–20 cc. of 0.5 *N* hydrochloric acid for 5–7 minutes. The cold filtrate is treated with a 1 per cent solution of picric acid until diphenylguanidine picrate has been precipitated. Extraction with hydrochloric acid for the determination of diphenylguanidine is made only when the sample is a mixture of accelerators or a combination of accelerators contained in a rubber compound. Mercaptobenzothiazole and tetramethylthiuram disulfide do not react with picric acid in hydrochloric acid solution, and therefore, do not interfere with the reaction for diphenylguanidine.

III. The Reaction of the Accelerators K-1 and A-19 with Sodium Hypochlorite and Phenol

(a) *Aqueous Extract.*—On the addition of 1 cc. of sodium hypochlorite solution and 2 cc. of phenol solution to the cold filtered aqueous extract of accelerator A-19, a bright blue color appears, either immediately or after standing for 3–5 minutes. The reaction is sensitive to 0.004 milligram of accelerator. The reaction depends on the decomposition of accelerators A-19 and K-1 on boiling in water or in an acid, with the liberation of aniline.

(b) *Hydrochloric Acid Extract.*—This procedure is used for the determination of small quantities of the accelerators A-19 and K-1 in rubber mixtures. A sample of 5–7 grams of rubber mixture is boiled with 0.5 *N* hydrochloric acid. The test is carried out in the same manner as with the aqueous extract, but in an exactly neutral medium. To this end, the extract is approximately neutralized with 0.5 *N* sodium hydroxide, and is then titrated with 0.1 *N* sodium hydroxide, with methyl orange as indicator.

IV. The Reaction of Mercaptobenzothiazole with Silver Nitrate

(a) *Ammoniacal Solution.*—A sample of 0.5 gram of accelerator is shaken with 15–20 cc. of 10 per cent solution of ammonia and filtered. The filtrate is treated with 2 per cent solution of silver nitrate until a flocculent precipitate of the silver salt of mercaptobenzothiazole is formed. The addition of an excess of AgNO_3 should be avoided, because it causes a dark discoloration in the solution.

(b) *Determination of Mercaptobenzothiazole in Acetone Extract.*—Approximately 10–15 grams of finely shredded rubber mixture are extracted with acetone in a Soxhlet apparatus for 40 minutes. After distillation of the acetone, the dry residue

is gently heated with 15–20 cc. of 25 per cent ammonia solution. The cool solution is then treated with 5 grams of sodium chloride to precipitate resinous impurities. The filtrate is treated with 2–3 cc. of 2 per cent silver nitrate solution until separation of the silver salt of mercaptobenzothiazole is complete.

ANALYTICAL PROCEDURE FOR THE DETECTION OF ACCELERATORS

A. Assay of Mixtures of Accelerators

The order of the qualitative detection of accelerators in unknown mixtures is as follows:

1. If the preliminary reaction of a benzene solution of the mixture with a benzene solution of cobalt oleate gives an insufficiently clear color reaction, this indicates the presence of impurities and also the preponderance of one or another accelerator in the mixture (see above under I (a)).

If the preliminary test does not give a conclusive answer, it is necessary to proceed with the tests described above under I (b) and (c), II (a) and (b), and IV (a).

2. Reactions I (b) and I (c) disclose the presence of diphenylguanidine, mercaptobenzothiazole, and tetramethylthiuram disulfide.

3. Reactions II (a) and II (b) are used for confirming the presence of diphenylguanidine.

4. Finally reaction IV (a) is applied to detect the presence of mercaptobenzothiazole, because in a mixture containing all three accelerators, the color reaction of mercaptobenzothiazole may be disguised.

B. Analytical Procedure for the Determination of Accelerators in the Base Mixture

Preparation of Sample for the Test.—The determination is chiefly made with aqueous extracts. A sample of 2–3 grams of finely shredded accelerator base mixture in 15–20 cc. of water is boiled for 5–7 minutes. The analytical procedure is very similar to that given above under A, but with the omission of reaction I (a). For the determination of the accelerators K-1 and A-19, reaction III is introduced.

The possible order of tests is as follows: Reactions I (b) and I (c) indicate the presence of all three accelerators (diphenylguanidine, mercaptobenzothiazole, and tetramethylthiuram disulfide).

In case of a mixture of tetramethylthiuram disulfide and mercaptobenzothiazole, the latter may be masked in reaction I (b). The presence of mercaptobenzothiazole in this case can be detected either by reaction IV (b) or by the color reaction with a benzene solution of cobalt oleate in the alcoholic extract. The latter test is carried out by refluxing 2–3 grams of finely shredded base mixture with 10 cc. of grain alcohol on a boiling water bath for 7–10 minutes. The cold filtrate is then treated dropwise with a benzene solution of cobalt oleate until a green color appears.

Reactions II (a) and II (b) are used to confirm the presence of diphenylguanidine.

The presence of accelerators K-1 and A-19 is detected by reaction III (a).

C. Analytical Procedure for the Detection of Accelerators in Rubber Mixtures

Preparation of Samples of Rubber Mixtures:

Aqueous Extract.—A sample of 5–7 grams of finely shredded rubber mixture is boiled with 15–20 cc. of water. For rubber mixtures containing 0.01–0.1 per cent of accelerator, a sample of 30–35 grams is used.

Hydrochloric Acid Extract.—A sample of 5–7 grams of finely shredded rubber compound is boiled with 15–20 cc. of 0.5 N hydrochloric acid solution.

Acetone Extract for the Detection of Mercaptobenzothiazole.—The mercaptobenzothiazole is extracted by boiling 10–15 grams of finely shredded rubber mixture with acetone for $\frac{3}{4}$ to 1 hour. The analysis is made by the reaction described above.

NOTE: Small quantities of mercaptobenzothiazole cannot be detected by the color reaction.

The following order of reactions in the detection of accelerators in a rubber mixture is used: Reactions I (b) and I (c) for the detection of either diphenylguanidine or tetramethylthiuram disulfide; reaction II (a) for the detection of diphenylguanidine; reaction II (b) for the detection of diphenylguanidine in all possible combinations of accelerators, since no other accelerators react in hydrochloric acid medium with picric acid.

Reactions III (a) and III (b) detect accelerators K-1 and A-19 individually and in all possible combinations.

Reaction IV (b) is used for the detection of mercaptobenzothiazole.

THE REAGENTS AND THEIR PREPARATION

The benzene solution of cobalt oleate is obtained by dissolving cobalt carbonate in oleic acid:

Cobalt carbonate can be obtained from any cobalt salt by the action of ammonium carbonate (10 grams of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 4–5 grams of ammonium carbonate). The precipitate is filtered, washed free from sulfate ion, and dried at a maximum temperature of 105°C . Five grams of cobalt carbonate are boiled with 25 grams of oleic acid until the mixture becomes cherry red. After cooling, the thick solution is dissolved in 100 cc. of pure benzene. Before using the solution, it is diluted with 20 parts of benzene. The solution should be kept in a glass-stoppered flask. It can be used as long as it remains cherry red. A decomposed solution of cobalt oleate acquires a brownish color.

Sodium hypochlorite is prepared by shaking 20 grams of chloride of lime with 100 cc. of water for 10 minutes. The filtrate is treated with 20 per cent solution of sodium carbonate until precipitation of calcium carbonate stops and is then filtered.

Phenol solution is prepared by dissolving 3 per cent of freshly redistilled phenol in water.

Tensile Tests with Flat (Straight) Test-Specimens

R. Ariano

1. Introduction

It is of course a well known fact that both ring test-specimens and flat or straight test-specimens are used in testing rubber. Ring test-specimens have for a long time been the most generally used type for testing rubber mixtures, whereas in American laboratories straight test-specimens are preferred.

Ring test-specimens are the more convenient to use, but they are open to one fundamental objection, that different parts of the cross section of the rubber are elongated to different extents at any particular moment.¹

Even straight test-specimens are not free from objectionable features. With this type of test-specimen, the inequality in the deformation at any particular instant results from the necessity of having enlarged ends for the testing machine to avoid breakage of the test-specimens in the jaws. It therefore becomes necessary to study systematically the form and dimensions of the end sections of the test-specimens and of the junction of these end sections with the central section, so that the points of rupture will not become localized in the sections in the jaws or close to these sections. As a matter of fact, an extensive investigation of this problem has been made by the Physical Testing Committee of the Rubber Division of the American Chemical Society.² By a proper study of the shape of the test-specimen, it is possible to design the test-specimen so that rupture occurs in the center section and therefore so that satisfactory tensile strength measurements are obtained.

However, the elongation at rupture and the stress-strain curve still remain to be determined. The first question is where to measure the elongation. If, as is convenient, the elongation is recorded directly, the elongation between the jaws of the testing machine is determined, but such measurements are of significance only if test-specimens of exactly standardized shape and dimensions are compared. This comparison is moreover quite arbitrary, and one has no right to ascribe any physical significance to the test, even if it is not complicated by slippage in the jaws and displacement of the original lines, which become ill defined if, as is frequently the case, eccentric jaws are employed.

All this is of interest, and those who attempt to draw up acceptable standardized methods of testing, with elimination of all doubtful factors, are always confronted with these difficulties. Then again there are times when it is necessary to test small thin strips of rubber removed from finished products, *e. g.*, tubing, belting, etc., and under these conditions resort must of course be had to straight test-specimens.

Finally it must be remembered that rubber is frequently chosen as a deformable material to aid in distributing the deformations which objects subjected to definite stress undergo.

Such a view of the problems of testing rubber seems to warrant a study of the distribution of deformations in a longitudinal direction along flat, straight test-specimens under stress, whether or not they are molded.

2. Results of the Tests

Figure 1 shows, in half-length sections, the shapes and chief dimensions of the test-specimens used in the investigation. These were died out of cured sheets prepared from a mixture of 100 parts of maturated (slab) rubber and 8 parts of sulfur, vulcanized in a press for 40 minutes at 143° C.

It is evident that the five forms of test-specimens had the following distinguishing characteristics:

- Type (a) a simple strip with straight sides.
- (b) a short specimen with relatively long intermediate section between the wide and narrow parts.
- (c) the same general type as (b) but with a shorter intermediate section.
- (d) the same general type as (c) but with longer intermediate section.
- (e) a specimen without intermediate section, with sudden increase in width from the ends to the central section.

On each test-specimen a latticework of parallel and perpendicular lines, one set of lines parallel to the direction of strain, the other set at right angles to this direction, were drawn. These marked specimens were photographed before and after elongating. By means of a projector the negatives were then enlarged, the necessary measurements were made, and the local deformations were calculated.

Some results of these calculations are reproduced in Fig. 1; in this diagram the average deformations along the lines in the direction of stress are recorded.

It is evident at once that the distribution of the elongations in the direction of stress, and therefore also the distribution of the transverse contractions (which are not included for the sake of simplicity and because the smaller measurements are less precise) differ with the shapes of the test-specimens.

In test-specimen (a), *i. e.*, without enlarged ends, the elongation near the jaws takes a wavy course, with maximum deformation in the jaws. If for no other reason, it is obvious that this simple distribution of the deformations should lead to rupture on a straight line along the extreme edge of the jaw. In such cases, elongation at rupture, particularly if short test-specimens are employed, has no significance.

In test-specimens of type (c), *i. e.*, in which the flared sections are short, the zone of maximum deformation tends to establish itself near the ends of the flared sections; in fact it is known that with this type of test-specimen measurements of rupture may be made readily in the flared section between the enlarged ends and the central parallelopiped-shaped section. The differences in elongation between the enlarged ends and the center section are so great that they require no comment.

In the case of test-specimens of type (d), *i. e.*, like type (c) but with longer flaring sections, these differences are very great, and it is therefore logical to assume that the point of rupture is displaced towards the central section, but likewise it is reasonable to attach no significance to elongation measurements if this rupture is not localized.

This subject has been studied by the present author in tests made in connection with another investigation,³ but such a technic could not be made readily adaptable to ordinary control testing, particularly if it were desired to avoid interrupting the stress, as may be necessary, not only for practical reasons but also because with some types of vulcanized rubber mixtures complications arise from abnormal plastic flow, and these may increase the differences.

The sudden change in width of the cross section of test-specimens of type (e) results in a maximum deformation close to this boundary line itself.

scale for test-specimen A



A



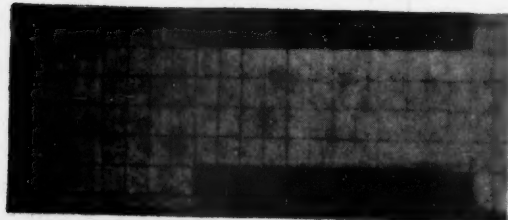
B



C



D



E



scale for test-specimen E

Test-specimens before stretching

Test-specimen B stretched



Figure 2

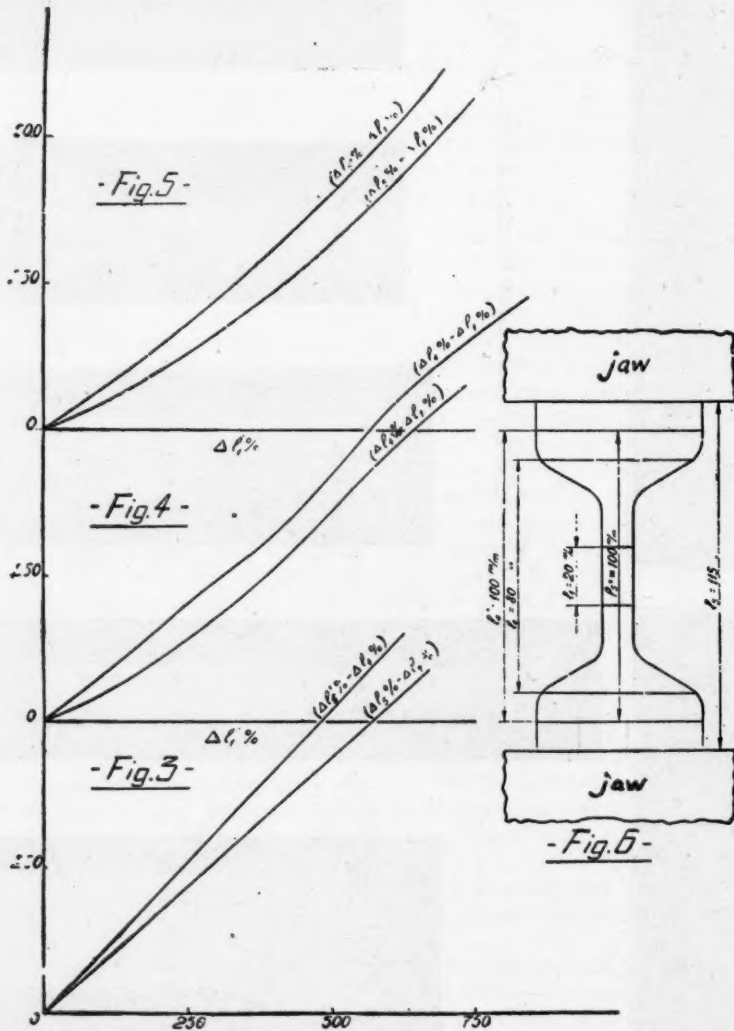
Test-specimen C stretched



In Fig. 2 it can be plainly seen that the closer the transverse lines lie to the jaws, the more curved they are.

3. Cases of Ambiguity Which May Arise by Not Taking into Account the Observations Described in Section 2

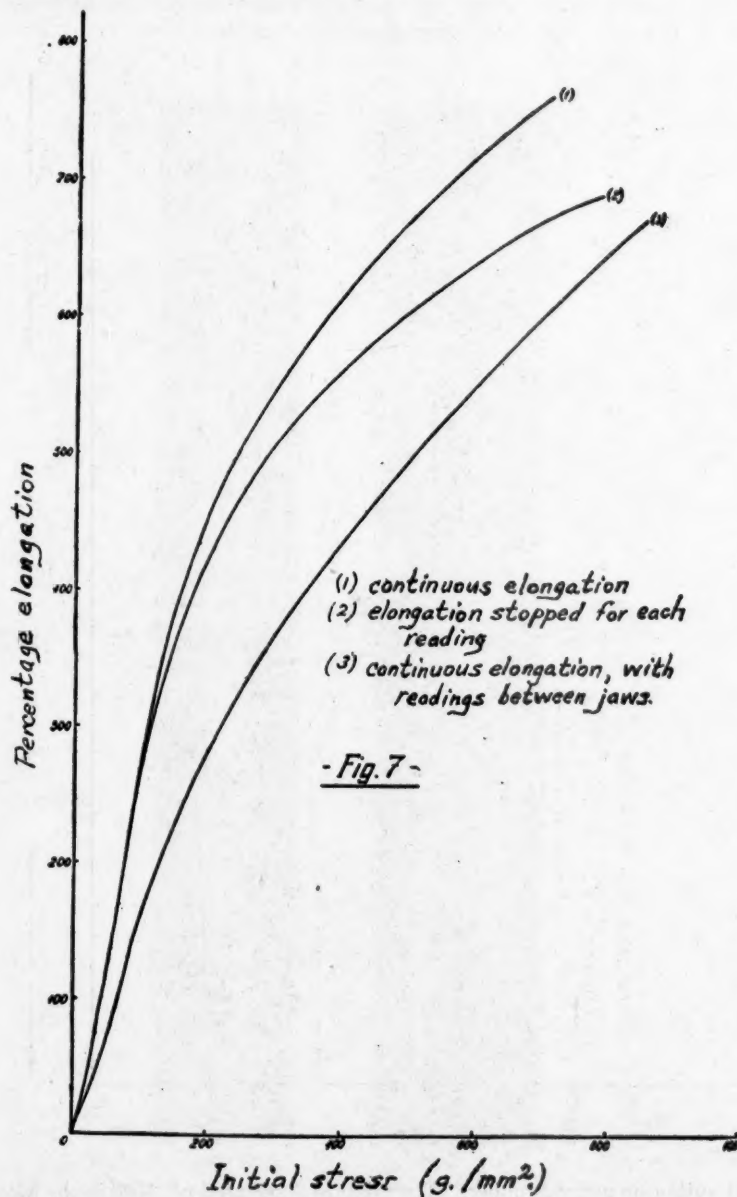
Figures 3, 4, and 5 show the relations which are found when elongations are measured between prefixed points on a test-specimen having the shape and dimen-



sions in Fig. 6. Next to each curve are shown in parentheses the meaning of the measurements recorded on the coordinate axes.

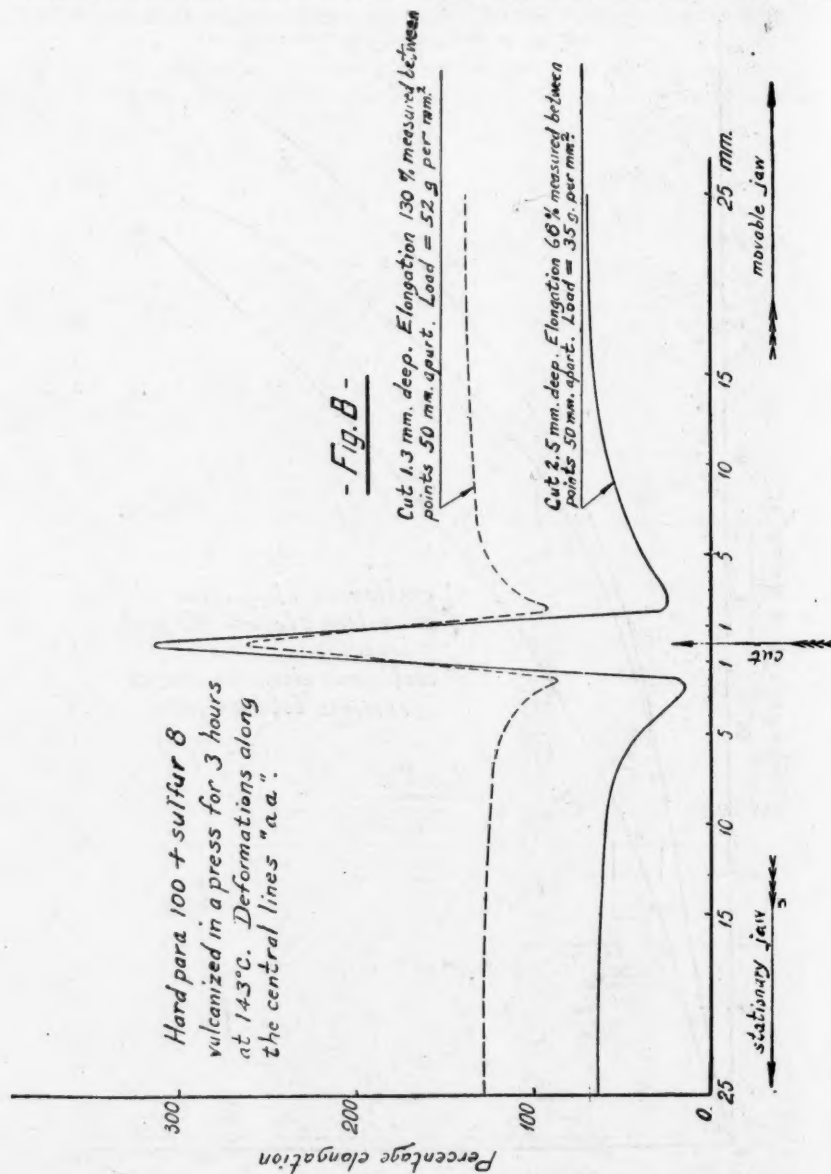
There is no need to analyze the results critically, in fact it is sufficient to point out by way of example that when a certain distance in the central section has elon-

gated, let us say, 500 per cent, according to the markings, the elongations as measured between the jaws are much less, *e. g.*, only 325 per cent.



It should be mentioned that these last tests were made on samples prepared from a synthetic substitute for rubber, *viz.*, Neoprene, because it was found in a surprising

way that the curves described in the Manual of E. I. du Pont de Nemours and Company do not follow the same course as that indicated in the early studies of the



present author on natural rubber. The mixture designated no. 1060 in the Manual in question contained 20 per cent of litharge and 10 per cent of magnesium oxide.

In Fig. 7 are shown: (1) A curve of the results of continuous stress on a Scott dynamometer with automatic registration, the data being that of the preceding

figures, the elongations being measured in the central section. The stress-strain curve has a course similar in general to that of natural rubber.

(2) A curve obtained in the same way as above, but with frequent stops to measure the stresses and corresponding elongations. This curve is in effect a

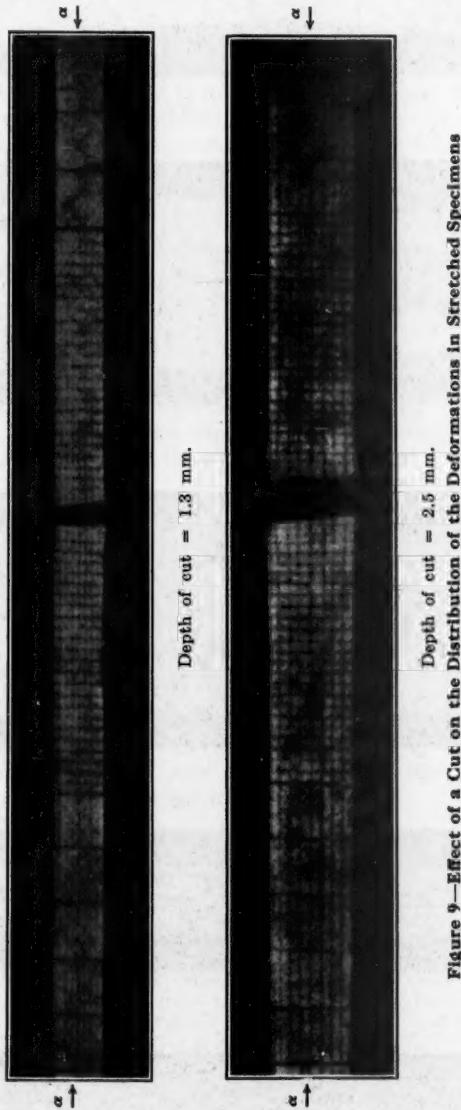
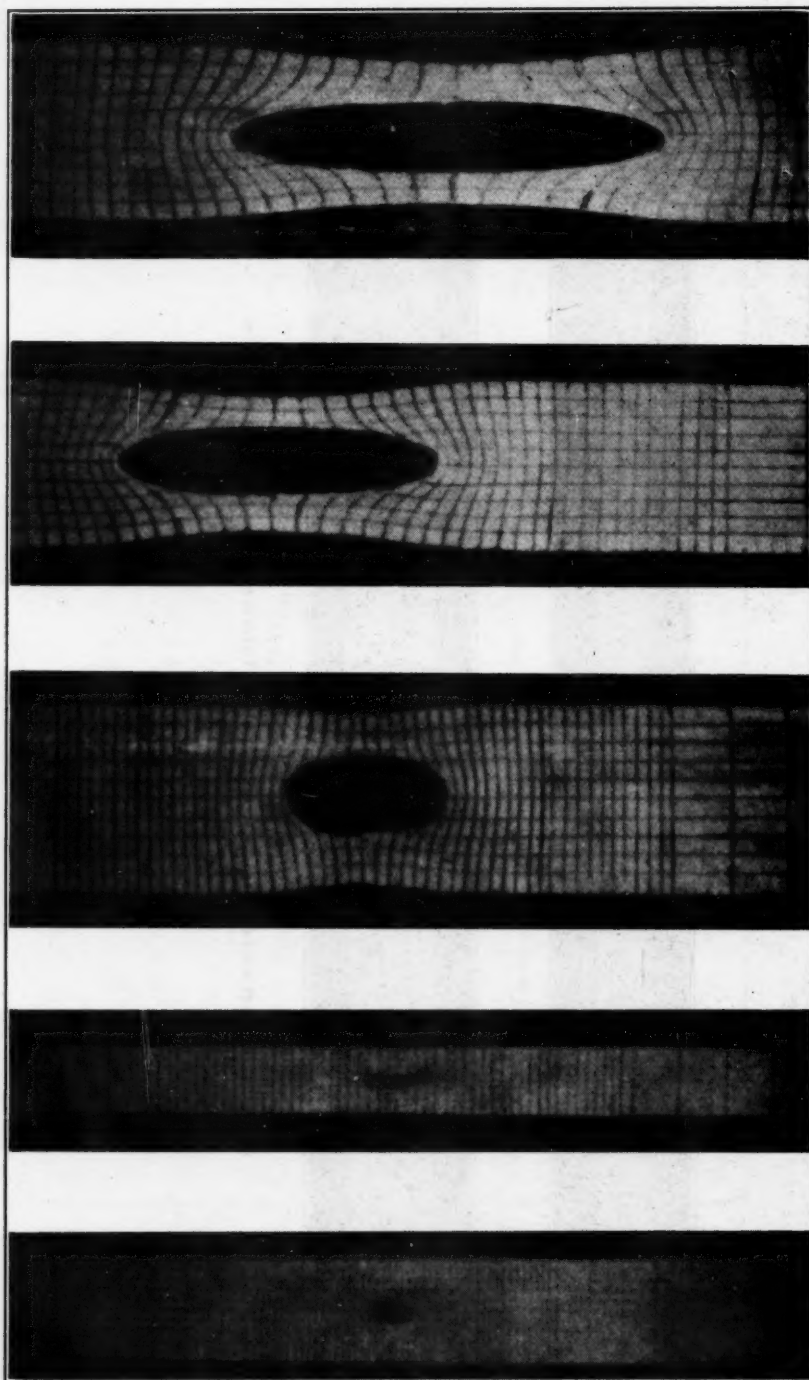


Figure 9—Effect of a Cut on the Distribution of the Deformations in Stretched Specimens

stress-strain curve of slow intermittent traction, and it shows the influence of the rapidity of elongation which, as has been demonstrated in earlier work of the author, is evident by a decrease in the elongation reached at any given stress.



$\phi = 2 \text{ mm.}$
 $\phi = 10 \text{ mm.}$

Figure 10—Effects of a Hole on the Distribution of the Deformations in Stretched Test-Specimens

(3) A third curve, which coincides with that shown in the Manual of E. I. du Pont de Nemours and Company, and which represents the elongations of the molded test-specimen measured between the jaws.

It is evident from this that the data in the Manual of E. I. du Pont de Nemours and Company are limited in their significance strictly to empirical comparisons.

4. Influence of Cuts in Test-Specimens

A study of the effects of cuts existing in test-specimens is of interest because it gives an idea of the trouble caused in testing by the presence of small cuts, and also because it gives a clue to the possible existence of local tears around a cut.

Figure 8 shows the local elongations measured along the middle lines of the test-specimens, which are shown under tension in Fig. 9. These test-specimens were 6 mm. thick, and they had very thin cuts, 1.3 mm. deep in one case and 2.5 mm. deep in the other case, which were made with a razor blade.

From Fig. 9 it is quite evident that the zones in proximity to the cuts are, for distances of 7-10 mm. on each side, less deformed than the remaining areas, in fact the differences are truly remarkable.

In a certain sense the cut section, when it opens, takes over by this very act, part of the deformation of the nearby zones. In conformity with the presence of a cut, the average elongation is notably increased. It is also evident that the slightest eccentricity in the application of the stress, *e. g.*, as a result of the jaws not squeezing the test-specimen uniformly across their entire width, is manifest not only by the lack of parallelism of the edges of the incision but also by the pronounced distortion of the zones close to the incision.

Figure 10 is a series of photographs of test-specimens in which holes were made in the centers of the straight sections, and the specimens were then stretched. The original diameters (ϕ) of the holes are shown below the photographs.

It will be seen that on the axis of each hole and in proximity to the hole, the elongation is much less, while along the sides of the hole it is abnormally great. Furthermore the face of the test-specimen does not remain flat and the longitudinal edges become curved inwards, so that the total width across the area where the hole lies becomes less. We believe that this explains the tear which appears in the cut section and that in the middle of the hole.

All this is readily understood, and our tests attempt only to prove the existence of localized deformations and to point out the extent of these irregularities in the geometric distribution of the elongation values.

References

¹ The objections to this type and a special discussion of the subject are to be found in a U. S. Bureau of Standards publication. It will also be helpful to consult a recent paper by Reece on "The Tensile Strength of Vulcanized Rubber," published in the *Transactions of the Institution of the Rubber Industry*, October, 1935.

² Cf. *Ind. Eng. Chem.*, May, 1925, 535; also Reece, see Note 1.

³ Ariano, "The Tensile Properties of Vulcanized Rubber," *Nuovo cemento*, 1925, p. 26.

The Falling-Weight Impact Test for Ebonite

H. F. Church and H. A. Daynes

INTRODUCTION

Many solid insulating materials which are quite strong under static loads or slowly applied stresses break readily when subjected to sudden mechanical shock. Thus, a poor quality molding may be reasonably strong under ordinary circumstances but may be shattered if dropped onto a hard surface or given a sharp knock. Such materials are said to be brittle, and the ability of materials to withstand rapidly applied blows is termed toughness or impact resistance. The liability of materials to chip when being machined is probably connected with the same factors as the tendency to brittleness.

The impact resistance or impact strength of materials is measured quantitatively either by determining the minimum energy in foot-pounds or kilogram-centimeters which is required to fracture a test-piece of given dimensions when struck in a defined manner by a high-speed blow, or by determining the energy absorbed in effecting such a fracture.

The results obtained when such tests are made in the laboratory are, however, found to be dependent on arbitrary conditions of test, such as size and shape of test-piece and velocity of impact, and no satisfactory method exists for expressing the property in absolute units as a constant of the material for use in designing. Different materials are affected in different ways by the same change in the test conditions, and it must be concluded that, before it is possible to make comparisons between materials, the test conditions must be rigidly standardized. Furthermore, if the figures obtained are to have any application to design problems, it is necessary to provide several different forms of standard test, the most appropriate being selected according to the proposed conditions of use.

Although there is no general agreement as to the best methods to apply to insulating materials, the specimen adopted is usually in the form of a rectangular bar supported in either of the following two ways and struck as described:

Charpy Support.—A bar resting against two supports, one near each end, and the blow applied at the center.

Izod Support.—A bar clamped rigidly as a cantilever, the blow being applied near the free end of the specimen.

In either case, the specimen may be plain or may be provided with a notch, and different shapes and sizes of notch are recommended by different authorities. The notch in the Charpy type of specimen is placed at the center across the face opposite that struck by the blow, whereas in the Izod type of specimen the notch is situated at the edge of the clamp across the struck face. The notch causes a concentration of stress in its immediate neighborhood, and causes a considerable reduction in the limiting blow which most materials can withstand. On the other hand, a few materials, particularly those having a laminated structure in the direction of the length of the specimen, are not so greatly affected by the presence of a notch.

The effect of notching has an obvious bearing on questions of the design of moldings and the like intended to withstand shock.

Although the results obtained in a suitably chosen standard test are exceedingly useful for making comparisons between various materials, manufacturers of special parts in which resistance to impact is important will usually find it advisable to supplement the tests on standard specimens by performance tests on the finished articles.

Types of Apparatus Available for Impact Testing

Two types of apparatus for carrying out the tests are available: the pendulum machine, and the falling weight apparatus.

Pendulum Machine.—In the pendulum machine the specimen is struck by a moving pendulum and the energy absorbed in fracture is measured by observation of the difference between the kinetic energy in the pendulum before impact and that in the pendulum after impact: that is, by comparing the height from which the pendulum was dropped onto the specimen and the height to which it rises after breaking the specimen. A value in foot-pounds of energy is obtained for each specimen tested.

Falling Weight Apparatus.—In the falling weight apparatus a weight is dropped onto the specimen with known kinetic energy, and it is observed whether or not the specimen breaks or is damaged. No measurement of the excess energy in the striker after fracture is made, but useful information can be obtained by testing a series of specimens with various blows.

In the course of a systematic investigation on ebonite which is being conducted by the Research Association of British Rubber Manufacturers in coöperation with the British Electrical and Allied Industries Research Association, a comparison of the impact strengths of a variety of ebonites became necessary.

After some consideration, the method ultimately chosen was that using the falling weight apparatus and Charpy type specimens, both unnotched and notched. The choice was based mainly on the following considerations.

The pendulum machine is the only one capable of measuring the total amount of energy absorbed during fracture, and it gives this result with a comparatively small number of specimens, as a definite result is obtained on each specimen. This result, however, is complicated by a number of factors, such as kinetic energy of flying fragments, and energy absorbed in separating the surfaces, which are only concerned with the phase of fracture after the first permanent damage has occurred. These factors are, therefore, to some extent irrelevant in an investigation of the minimum energy to cause fracture or damage, which is the property of real practical significance.

The pendulum machine may be used in the same way as the falling weight machine to determine the minimum energy for break as described below. Used in this way it requires about the same number of specimens as the falling weight machine, except that a few specimens are saved owing to the indication of excess energy which it gives during preliminary tests. This advantage, however, was not considered to outweigh the greater difficulty and expense of making a suitable pendulum machine.

In this paper, the falling weight apparatus constructed for the ebonite research and the technic developed for its use are described.

Description of Falling Weight Machine

The machine specially designed and constructed for the research is illustrated in Fig. 1.

Briefly, it consists of a knife edge which is weighted and allowed to fall vertically between guides from a known height onto the center of a straight strip of the mate-

rial under test, the strip being supported in a horizontal position on two parallel fixed knife edges near its ends.

The constructional details of the apparatus are as follows: The two parallel fixed knife edges (2, 2'), are firmly bolted to a heavy iron base (1) and are of equal height and 5.08 cm. (2 in.) apart, the edges being rounded to 1.6 mm. ($\frac{1}{16}$ inch) radius. Between the knife edges are fixed vertically two parallel straight steel runners (3, 3'), held together at their upper extremities by a spacing piece. A weight carrier attached to the center knife edge (4) consists of a disc (5) attached to a ring (6) by three equally spaced rods, a light release rod (7) being fixed to the center of disc (5). The carrier weighs 250 grams, and a series of cylindrical weights (8), each provided with an axial hole, may be slipped onto the rod (7) to give any desired total weight between 250 grams, and 2250 grams, the weights being held in place by a collar (10). The carrier can slide freely, but with the minimum of play, between the runners, the latter being so placed as to direct the knife edge (4) exactly midway between and parallel to the fixed knife edges. The moving knife edge is rounded to 3.2 mm. ($\frac{1}{8}$ in.) radius.

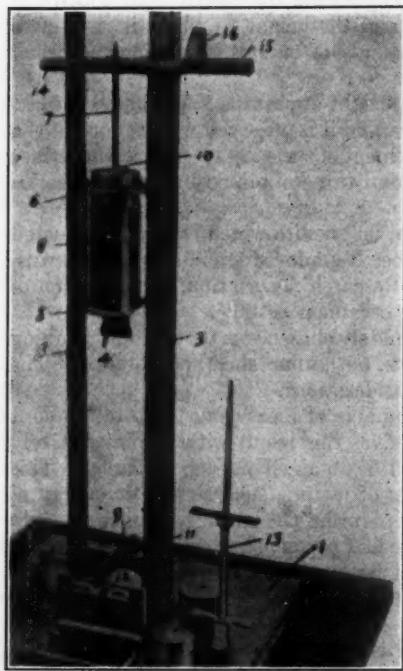


Figure 1

The test-piece (9) is placed centrally across the fixed knife edges by means of guides (11) which are adjustable in position according to the thickness of the test-piece. Usually no adjustment is required as the test-piece is normally of standard width. The same guides, in conjunction with marks on the test-piece, afford the means of adjustment of the notched test-piece so that the notch is immediately beneath the center of the moving knife edge.

A thick pad of rubber between and a little below the fixed knife edges arrests the falling carrier after impact and prevents damage to the apparatus.

When it is desired to use a total load of less than 250 grams, as is usual with notched test-pieces, a light carrier (13) weighing only 70 grams is employed. This carrier would be damaged by the use of weights much in excess of 250 grams. A third carrier of aluminum, weighing only 37 grams, has also been used.

The platform (15) from which the carrier can be released with zero initial velocity is movable in position so that the height of fall of the carrier is continuously variable between 0 and 60 cm.

Dimensions of Test-Pieces.—In selecting a suitable size of test-piece for the present research, one dimension was necessarily fixed, as all specimens have to be machined from molded sheet approximately 5 mm. thick. As this dimension was rather variable, it was decided to make it the width of the impact specimen rather than

the depth, it having been found that it was necessary to standardize the latter dimension fairly exactly.

The other dimensions of the test-piece adopted were as follows:

Unnotched test-piece: Length, 75 mm. (3 in.).
Depth, 12.7 mm. ($1\frac{1}{2}$ in.).
Notched test-piece: Length, 75 mm. (3 in.).
Depth, 19 mm. ($\frac{3}{4}$ in.).

The notch, which was placed centrally across the lower face of the test-piece, was 6.3 mm. ($\frac{1}{4}$ in.) in depth and was formed by drilling a 1.6 mm. diameter hole through the specimen and breaking through to the under-face by a saw cut. The cross-sectional area of both notched and unnotched specimens, it will be seen, is the same at the center. A special drilling jig was used in order to ensure that the notch was exactly the specified distance from the struck edge; simultaneously a mark was made on the specimen for the purpose of locating the specimen centrally between the knife edges with respect to the notch.

Methods of Use of the Falling Weight Apparatus

Method 1.—In this method the criterion of the impact strength is the energy of the blow which will break one-half the specimens submitted to it, each specimen being struck only once.

Usually thirty test-pieces are prepared and divided into sets of six, selected so as to eliminate the effects of any systematic variation in properties over the sheet from which they are cut. Each set is submitted to a different impact blow per unit area of section, the velocity of impact being fixed and the weight varied as required. A curve is then plotted showing the relation between energy of blow and percentage of breaks. The central portion of this curve is usually linear, though often rather irregular and inclined considerably to the vertical. The blow per unit area which would break one-half the specimens is estimated from the smoothed curve and is recorded as the impact strength. It is often found that a good value can be obtained with a small number of different impact blows, in which case the surplus samples may be redistributed to increase the number of tests at each value of the impact blow and so improve the accuracy.

Where possible, the height of fall of the weight is selected to give an impact velocity of 200 cm. per sec. (fall, 20.4 cm.), but with unnotched test-pieces of most pure ebonites 300 cm. per sec. (45.9 cm. fall) must be used, owing to the upper limit to the weight which can be used with this particular machine. The effect of varying the velocity of impact is considered later.

Some typical results are shown in Fig. 2.

B and *C* both represent fairly completely vulcanized ebonites, *B* being a rubber-sulfur (68:32) mixing, and *C* a rubber-sulfur (72:28) mixing. The values of impact strength read from the curves are:

B (unnotched)—52 kg. cm. per sq. cm.
C (unnotched)—83 kg. cm. per sq. cm.
C (notched) — 7 kg. cm. per sq. cm.

The figure attached to each point indicates the number of specimens tested at that value of blow.

The slope of the curve is related to the variability of the material. Thus, curve *B* (unnotched) indicates a more variable material than *C* (unnotched). The variability of a material is an important consideration in deciding upon its suitability for a certain application.

The disadvantage of this method of test is that a large number of test-pieces is necessary, requiring considerable material and time in preparation.

Method 2.—To increase the accuracy and at the same time economize in test-pieces, a modified method has been devised in which each test-piece is subjected to a series of blows of increasing magnitude until breakage occurs. This involves a departure from standard practice, in which each specimen is struck only once, but it does not appear to be an objectionable change, for if the strength of a material is greatly affected by a few previous blows, only one or two of which are comparable with the breaking blow, the information may be quite as valuable as the breaking strength for a single blow.

In the case of unnotched samples, a fixed weight is released successively from heights of 10, 20, 30, 40 cm., and so on until breakage occurs, the load being selected

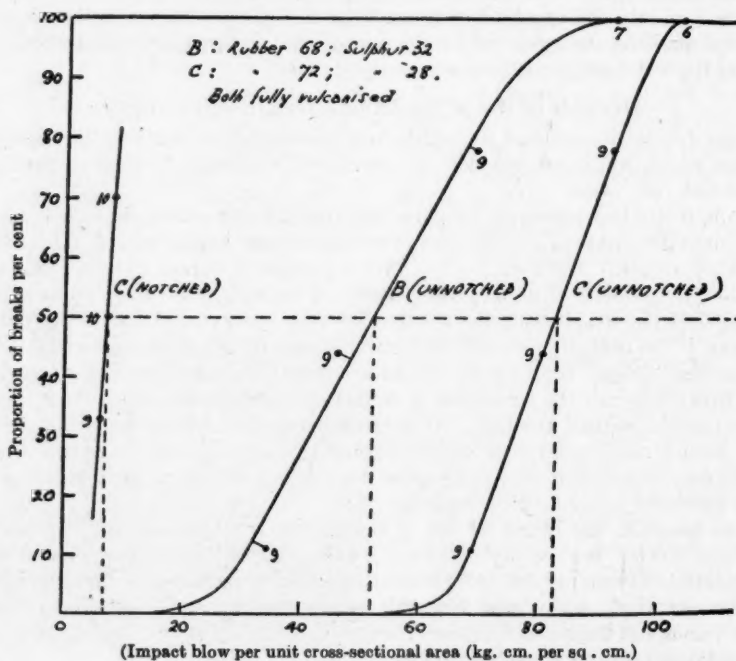


Figure 2—Proportion of Breaks under Various Impact Blows

by preliminary tests so that, on the average, one-half the specimens are fractured by a fall from a height of 40 cm. The results for different materials are thus comparable as to velocity of impact, a condition which previous writers have recommended as desirable. The impact strength of each sample is regarded as the product of the falling weight per unit area of cross section and the mean of the height which causes break and the preceding height of release. The impact strength of the material is taken as the mean of the impact strengths, so defined, of the individual samples.

The same method is used for notched samples except that the series of heights of fall is 5, 10, 15, 20, 25 cm., and so on, the load being selected so that, on the average, one-half the specimens are fractured by a fall from a height of 20 cm.

Generally with this method a reproducible result can be obtained with as few as 12 test-pieces, as the strength of each test-piece is known to within narrower limits than with the first method. Exact agreement between the two methods is not necessarily to be expected, as the fatigue factor enters into Method 2.

The effect of this fatigue factor was demonstrated by comparing the results of tests by the two methods on a range of ebonites composed of various proportions of rubber and sulfur and vulcanized for various periods. The mixings employed were: Rubber 65, sulfur 35 parts by weight; rubber 68, sulfur 32; and rubber 72, sulfur 28; all vulcanized for a range of time periods from 3 to 10.5 hours at 155° C. The mixing having the low sulfur content, *i. e.*, rubber 72, sulfur 28, was found to be considerably more resistant to impact than the other two mixings whether tested by Method 1 or by Method 2.

It was observed that Methods 1 and 2 gave almost identical results except for the low-sulfur mixing: in this case Method 2 gave results roughly 20 per cent lower than Method 1. The identity of results by the two methods held, whether notched or unnotched specimens were tested. The specimens of this mixing which just failed to break when tested by Method 1, using unnotched specimens, showed marked permanent distortion when examined some months after test. This distortion was measured by observing the displacement of the center of the test-piece. Practically no permanent set was shown by the other mixings and none by any of the notched specimens.

Thus, Method 2 appears to give a lower result than Method 1 with materials which distort considerably under blows less than that necessary to cause fracture. Method 2, therefore, has the advantage of taking into account to some extent the tendency to permanent deformation. This may be regarded as an advantage, as severe distortion is generally as serious as breakage.

Method 3.—In order, for some purposes, to emphasize the fatigue factor still more, the second method has been modified as follows: Each of the series of increasing blows obtained by increasing the height of fall is repeated to a total of six times before applying the next of the series, the load being selected and the impact strength calculated in the same way as in Method 2.

Results on three mixings mentioned above were much lower in all cases than by Methods 1 and 2, but the rubber-sulfur (72:28) material was still slightly superior.

Typical Results

Method 2, besides being economical and convenient in use, has been found to give more regular results than Method 1, and has been adopted as the usual test method for ebonite in the laboratories of the Research Association of British Rubber Manufacturers. Method 3 is regarded as one to be used only where the fatigue factor is to be emphasized.

Some interesting observations as to the three different methods and the differences between notched and unnotched test-pieces may be made by a study of some typical results obtained in the course of the joint investigation mentioned previously. These results which are shown in Table I, were obtained from fifteen samples of ebonite of different rubber-sulfur ratios and periods of vulcanization. All the samples were similarly vulcanized in sheets, first in a daylight press and finally in an autoclave press, but the test-pieces used for Methods 1, 2, and 3 were not necessarily taken from the same sheet.

An examination of Table I shows that all methods agree substantially as to the relative merits of the mixings and vulcanization times. For example, they all show an optimum vulcanization time with unnotched samples, and in general a continuous fall in strength on vulcanization with notched, except in the rubber-

sulfur (72:28) mixing, where the strength is maintained up to between 7 and 10.5 hours' vulcanization. The mixing having the lowest sulfur content has the highest impact strength with both notched and unnotched test-pieces.

TABLE I
IMPACT STRENGTHS OF RUBBER-SULFUR COMPOSITIONS
Impact Strength (Kg. Cm. per Sq. Cm.)

Ratio of Rubber to Sulfur	Vulcaniza- tion (Hrs. at 155° C.)	Impact Strength (Kg. Cm. per Sq. Cm.)					
		Unnotched, by Method:			Notched, by Method:		
		1	2	3	1	2	
65/35	3	33.3	40	32.5	3.32	3.6	
	3 ³ / ₄	56.3	55.5	2.86	2.05	
	5	56.4	55	38.4	2.28	2.0	
	7	52.2	46	5.80	1.7	
	10 ¹ / ₂	42.0	46.5	24	2.04	1.75	
68/32	3	66.0	33	24	3.88	3.7	
	3 ³ / ₄	66.0	60	2.36	2.8	
	5	57.9	56.5	41.7	3-4	2.1	
	7	53.7	59	2.70	2.05	
	10 ¹ / ₂	33.7	56	40	1.98	2.0	
72/28	3	62.2	66	42.5	5.22	4.0*	
	3 ³ / ₄	85.5	70	6.58	3.6	
	5	93.9	75	48.5	4.28	3.7	
	7	83.2	72	7.06	4.0	
	10 ¹ / ₂	83.0	61	43	2.5-3.0	2.9	

* Only 6 samples tested.

It is seen that the figures obtained on all these ebonites are very much lower when notched test-pieces are employed than when the specimens are unnotched. The ratio of unnotched to notched strength varies between about 11 and 29 according to the mixing and vulcanization. The ratio is very high with ebonite, owing to its great capacity for absorption of energy in the form of elastic strain, this absorption being more generally distributed throughout the test-piece in the unnotched sample.

Not many loaded ebonites have been tested for impact strength in this research, but it seems to be general that the usual powders incorporated in compounded ebonites cause a reduction in strength.

A general conclusion which may be made as a result of considerable experience of impact testing is that impact strength appears to be very sensitive to untraced variables in the material and the preparation of the test-pieces; it is often found that there is considerable variation between specimens taken from a single sheet, and still more between sheets or moldings of nominally the same composition and vulcanization but prepared at different times, even where the specimens are similar in respect of other mechanical properties.

INFLUENCE OF DIMENSIONS OF TEST-PIECE AND VELOCITY OF IMPACT

The dimensions of the test-piece and the approximate velocity of impact have been standardized, but it was necessary to investigate the effect of any deviations from these standard conditions in order to specify tolerances in testing and to correct for any considerable departure where it is impossible to adhere to standard conditions. The information should also be of interest from the theoretical point of view. Method 2 was used for these tests.

Dimensions of Unnotched Test-Piece

Two series of tests were carried out with unnotched test-pieces in which the depth and width, respectively, were varied, the other dimension and the distance between the knife edges remaining constant in each case.

Depth.—The material used was composed of 70 parts of rubber and 30 of sulfur, vulcanized for five hours at 155° C. The width of the test-piece and the average velocity of impact were kept constant at about 5.3 mm. and 280 cm. per sec., respectively, but the depth was varied between 6.5 and 18.9 mm. The effect of this variation of depth is shown by curve (1) of Fig. 3. It is observed that impact strength, in terms of energy per unit cross-sectional area of the specimen, is dependent on depth except when the depth is small relative to the distance between the

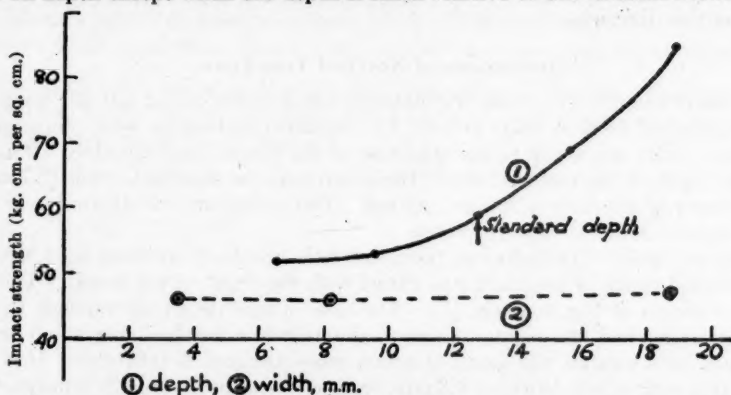


Figure 3—Effect on Impact Strength of Dimensions of Unnotched Test-Piece
 —●— Rubber 70, Sulfur 30 (vulcanized 5 hours at 155° C.)
 --(○)-- Commercial sample

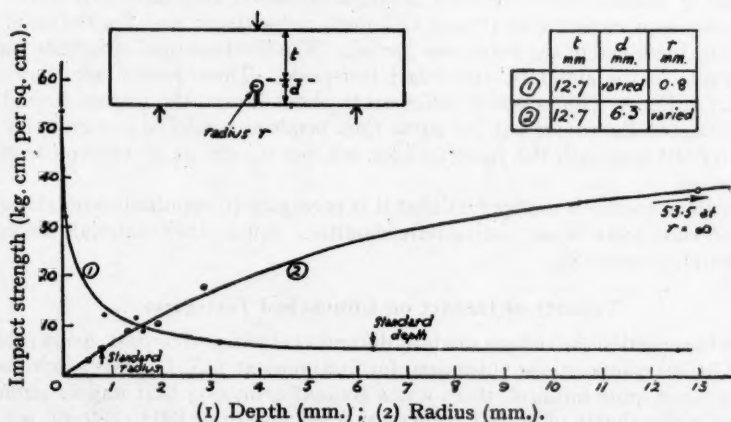


Figure 4—Effect on Impact Strength of (1) Depth and (2) Radius of Notch

knife edges, that is, when the depth is less than about one-fifth of the distance between the outer knife edges. It must be remembered that where the ratio of depth to length cannot be regarded as small, the simple elastic theory of a bent rod does not apply, owing to the complication of shear stresses, friction on the supporting knife edges, and so on.

With the particular standard depth adopted for ebonite testing (12.7 mm.) the results are not very sensitive to variations of depth from the agreed standard, but for accurate work it is clear that some care must be taken to machine the depth of the specimens to within fairly close limits.

Width.—Samples of the same ebonite of the required thickness were not available for these tests, so experiments were carried out with a thick sample of a good quality commercial ebonite. The depth was 10 mm. and the average velocity of impact 280 cm. per sec. Specimens were machined to various widths as required. The results are shown by curve (2) of Fig. 3 and it is seen that impact strength, as defined in terms of the breaking blow per sq. cm. of cross section, is independent of width over the whole range studied. Hence there is no need for accurate standardization of this dimension.

Dimensions of Notched Test-Piece

In both of the following tests the material was a rubber-sulfur (70:30) composition, vulcanized for five hours at 155° C. Notched test-pieces were prepared so that their width was equal to the thickness of the sheet (approximately 5.3 mm.) and the depth of the material above the notch had the standard value 12.7 mm. The velocity of impact was 200 cm. per sec. The variations investigated were the depth of notch and the radius of notch.

Depth of Notch.—The radius of the notch-hole was kept constant at 0.8 mm., and the total depth of specimen was varied with the depth of the notch. The results are shown in Fig. 4, curve (1). The case of zero depth corresponds to the standard unnotched test-piece. An approximation to a notch of very small depth was given by a scratch, the depth of which was estimated at 0.07 mm. It is observed that with notch depths of 6.3 mm. or more the impact strength is insensitive to variation of this depth. When, however, the depth is reduced to 3 mm. there is a noticeable increase, and thereafter the increase in sensitiveness is very rapid.

Radius of Notch-Hole.—The total depth of specimen and the depth above the notch were kept constant at 19 and 12.7 mm., respectively, and the radius of the hole at the inner end of the notch was varied. The limiting case of infinite radius corresponds to the standard unnotched test-piece. These results are shown by curve (2) of Fig. 4. For a notch radius up to about 3 mm. the impact strength is proportional to the radius but the curve then bends as would be expected, for the strength must approach the value 53.5 kg. cm. per sq. cm. as an asymptote at infinite radius.

From these results it is apparent that it is necessary to standardize notch radius to within close limits when testing pure ebonites. Some other materials are much less sensitive to notching.

Velocity of Impact on Unnotched Test-Piece

A few observations have been made at different velocities of impact, using rubber-sulfur (70:30) compositions vulcanized for five hours at 155° C. Although the results were not quite uniform, there was a general indication that impact strength increases with velocity of impact. Increasing velocity from 180 to 280 cm. per sec. caused an average increase of strength of roughly 10 per cent, a relatively small effect.

Summary

1. With unnotched test-pieces, although impact strength is uninfluenced by variations of width of test-piece, the depth must be fixed.
2. With notched test-pieces, impact strength is independent of the depth of the notch with deep notches, provided the depth of the material above the notch is kept constant. Impact strength is, however, very sensitive to variations of notch radius.

3. Impact strength increases slightly with velocity of the striker, so that this should be kept within reasonably narrow limits for accurate work.

4. The falling weight type of apparatus provides a simple and convenient method of testing the resistance of ebonite and similar materials to damage or fracture by impact.

5. Three variations of the method of use of this apparatus are described which involve the factor of fatigue to different extents.

6. Results with a number of pure ebonites of different compositions and vulcanization times are given to show the influence of those factors on impact strength.

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The T-50 Test Applied to Zinc Oxide Compounds

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THE function of zinc oxide in the vulcanization reaction and the effect of various modifications of zinc oxide on the curing rate of rubber compounds have received considerable attention. In the past few years, the development of a number of new grades of zinc oxide, having a wide range of chemical and physical properties, has served to increase the interest in this pigment and in methods of evaluating the effect of these several modifications in the laboratory.

Several methods of attack have been applied to studies of the effect of zinc oxide on the curing rate of rubber, ranging from the analytical determination of free and combined sulfur, through the conventional physical tests, to actual performance evaluation. This latter method is obviously the most satisfactory but is also the most costly and time-consuming. The use of physical measurements, such as stress-strain properties, has been the most widely used method of evaluating compounds, the principal objections being the inherent inaccuracies of rubber testing and the failure to differentiate between "state of cure" and the actual reinforcing value of the pigment.

In 1933, Gibbons, Gerke, and Tingey (1) published a discussion of a test method which they called the T-50 test. Since that time relatively little has been published, although it is known that the test is being used in a number of laboratories in a routine way. Inasmuch as this test is particularly sensitive to state of cure, following, in a general way at least, the combined sulfur analysis, it is obviously of real interest in studies of any factors affecting the curing rate. In this paper, the authors report their efforts to apply the T-50 test to a study of the effect of zinc oxide and zinc oxide variables on the curing rate of rubber compounds.

Discussion of Test Method

Briefly, the T-50 test consists of stretching a 1.5 by 0.075 inch strip of rubber to a predetermined elongation (500 per cent was used in all the tests reported in this paper); while in the extended position, the specimen is frozen at -70°C . in acetone, the temperature of which has been reduced by passing it through a coil immersed in solid carbon dioxide and acetone. The holder is released while the rubber is frozen, the acetone

bath is allowed to heat up, and the temperature at which the rubber regains its elastic properties is observed. The temperature at which the rubber has retracted to 50 per cent of its original elongation is known as the T-50.

The apparatus used is essentially the same as that described by the above-mentioned investigators and is shown in Figures 1 and 2. Figure 3 shows the redesigned specimen clamp, which, by eliminating the necessity for screwing the test piece in place increases the ease and speed with which the holder is loaded. An induction motor stirrer was sub-

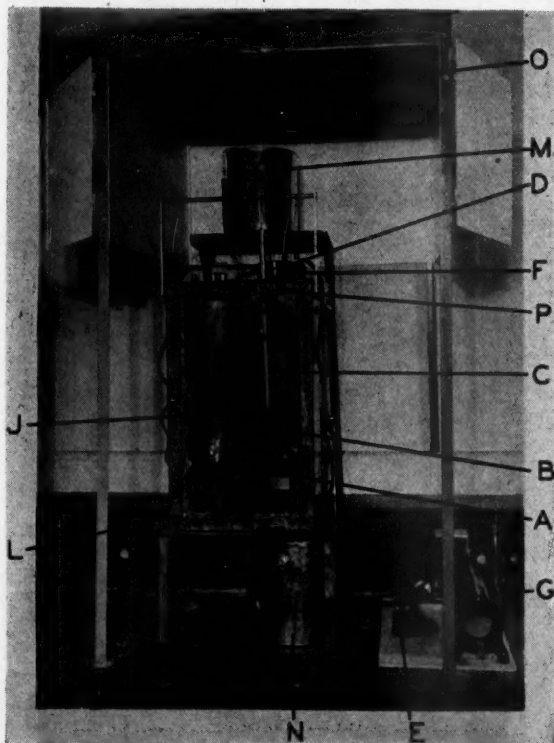


FIGURE 1. GENERAL ASSEMBLY OF APPARATUS

- | | |
|--------------------------|---------------------------|
| A. Testing Dewar flask | J. Insulated cooling tank |
| B. Specimen rack | L. Glass-windowed tank |
| C. Thermometer | M. Acetone reservoir |
| D. Stirrer | N. Acetone overflow |
| E. Stirrer speed control | O. Ventilated hood |
| F. Heater | P. Weights |
| G. Rheostat for heater | |

stituted for the remote-driven stirrer of the original apparatus.

In order to obtain a satisfactory value to express curing rate, an extensive study of the time of cure versus T-50 curve was made. In all cases a compound having a T-50 of -7°C . was a satisfactorily cured stock. In order to condense the

data and to use a single value for the expression of rate of cure, it was decided to express the results in terms of the time of cure in minutes to give a T-50 of -7°C . This value was obtained by plotting the T-50 for a range of cures, drawing a smooth curve through these points, and interpolating the time at -7°C .

This value should not be interpreted as the optimum cure, but rather as the length of time required for a specified stock to reach a definite state of cure. By this means, the curve of time of cure versus T-50 is reduced

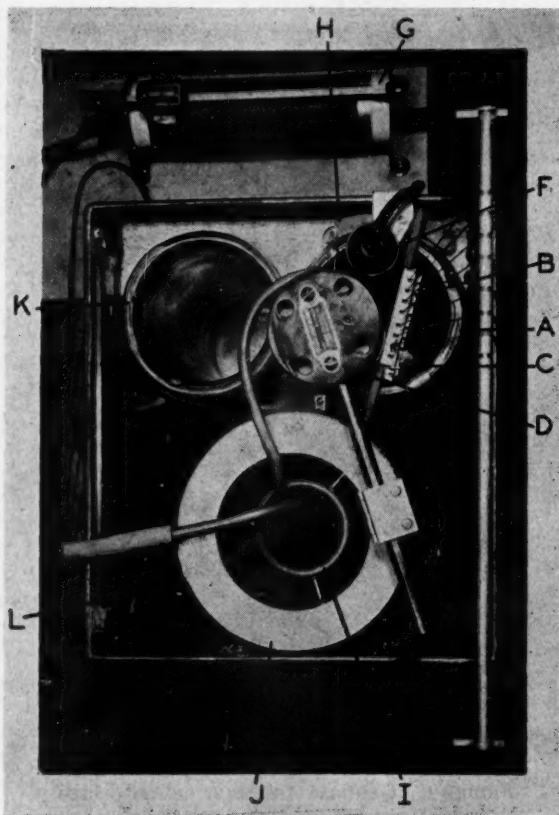


FIGURE 2. TOP VIEW OF APPARATUS

- | | |
|------------------------|-----------------------------|
| A. Testing Dewar flask | H. Siphon overflow |
| B. Specimen rack | I. Copper cooling coil |
| C. Thermometer | J. Insulated cooling tank |
| D. Stirrer | K. Conditioning Dewar flask |
| F. Heater | L. Glass-windowed tank |
| G. Rheostat for heater | |

to a single value, the accuracy of which is greater by virtue of the fact that it is essentially an average of 6 determinations rather than one. Physical tests and performance evaluation will still have to be used to establish the optimum for each different compound.

Some difficulty was encountered in reaching and holding a temperature of -70°C. , particularly on days when the labo-

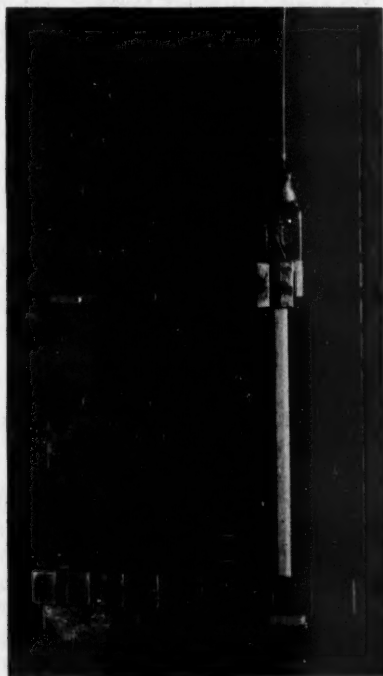


FIGURE 3. CLOSE-UP OF SPECIMEN HOLDER

ratory temperature was high. As a matter of interest, a series of tests was carried out using freezing temperatures of -70° and -50°C. The data obtained are shown in Table

TABLE I. EFFECT OF FREEZING TEMPERATURE
(Compound 4, Z. M. L.)

	Cure at 30 lb. Min.	-70°C.			-50°C.		
		1st test	2nd test	Av.	1st test	2nd test	Av.
Compound contain- ing 5 parts zinc oxide A	15	+ 2.0	+ 1.0	+ 1.5	+ 2.5	*	+ 2.5
	30	-10.5	-11.5	-11.0	-11.5	-11.5	-11.5
	45	-20.0	-18.5	-19.6	-21.0	-20.0	-20.5
	60	-26.5	-25.0	-25.8	-26.5	-25.0	-25.8
	90	-35.0	-31.0	-33.0	-33.0	-30.5	-31.8
	120	-40.0	-33.5	-36.8	-35.5	-33.5	-34.5
Time to T-50 of -7°C.		26.0	25.5	26.0	26.0	26.0	26.0
Compound contain- ing 200 parts zinc oxide A	15	+ 9.0	+ 8.5	+ 8.8	+ 9.0	+ 9.5	+ 9.3
	30	+ 1.5	+ 0.5	+ 1.0	0	+ 2.0	+ 1.0
	45	- 7.0	- 7.5	- 7.3	- 7.0	- 7.0	- 7.0
	60	-12.5	-12.5	-12.5	-12.0	-12.0	-12.0
	90	-20.0	-19.0	-19.5	-19.5	-19.5	-19.5
	120	-23.0	-22.0	-22.5	-22.0	-21.5	-21.8
Time to T-50 of -7°C.		45	44	44.5	45	45	45

* Unhook.

1. As these data indicate that in the present investigation the starting temperature was not particularly important, a compromise was made. In every case the acetone temperature was reduced to at least -65°C ., but no effort was made to obtain exactly -70°C . as did the investigators mentioned above.

TABLE II. REPRODUCIBILITY OF RESULTS

(Compound 1: Captax with 50 parts zinc oxide A)

Cure	Days of Shelf Aging														Av. of 10 Tests
	1		3		7		9		15						
5	+ 9.0	+ 9.5	+11.0	+10.3	+11.0	+10.3	+10.5	+10.3	+ 8.5	+ 7.5	+ 7.5	+ 9.8			
10	+ 1.0	+ 4.0	+ 6.0	+ 1.5	+ 2.8	+ 3.5	+ 3.0	+ 2.5	+ 2.0	+ 1.0	+ 1.0	+ 2.7			
15	- 3.5	- 3.0	- 2.0	- 3.5	- 2.5	- 3.3	- 2.5	- 4.0	- 4.3	- 5.2	- 3.4				
30	-17.0	-17.0	-17.0	-17.3	-16.3	-17.0	-17.0	-17.5	-16.0	-18.0	-17.0				
45	-24.5	-25.5	-26.5	-26.0	-25.5	-25.8	-25.8	-26.0	-25.8	-26.5	-25.8				
60	-29.0	-29.0	-31.0	-30.0	-28.5	-32.3	-29.5	-30.0	-28.5	-30.0	-29.8				
*	16.5	-17.0	19.0	16.5	17.5	17.5	17.0	17.0	18.0	17.0	17.3				

* Time of cure (minutes) to T-50 of -7°C .

It was also desirable to determine what effect shelf aging over a period of a week or 10 days might have on the T-50 results. One compound was selected and run in duplicate with 3- or 4-day intervals between determinations. These data are shown in Table II and indicate that the reproducibility between the first and after 14 days is as good as that obtained on any one day. All results herein reported were run on compounds which were cured at least 24 hours before the test and none was held more than a week after curing.

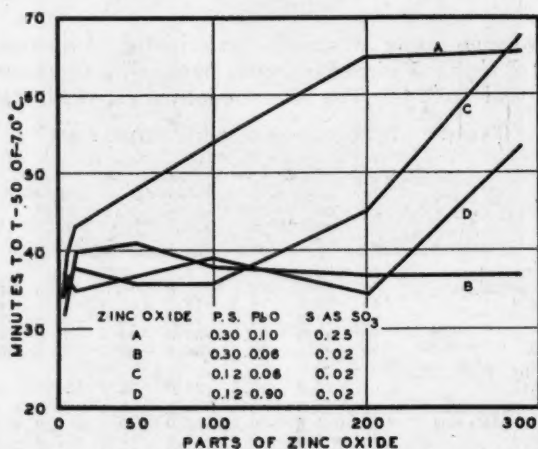


FIGURE 4. TESTS ON COMPOUND 1, CAPTAX

Summarizing, all tests were carried out using an initial elongation of 500 per cent, a freezing temperature of less than

-65° C., and a shelf-aging period of at least 1 day but not more than 7 days. All results wherever possible are expressed in terms of time of cure in minutes to give a T-50 of -7° C.

Discussion of Results

For this preliminary survey, 4 standard zinc oxides representing modifications of particle size, lead, and sulfur content were chosen. Zinc oxide *A* is a slow-curing oxide and zinc oxide *B* is a fast-curing oxide of essentially the same particle size. Zinc oxides *C* and *D* are oxides of fine particle size, the former being essentially lead-free and the latter containing approximately 1 per cent of lead as the oxide which has an accelerating effect particularly evident with certain accelerators. The particle sizes and chemical analyses of these oxides are given in Table III.

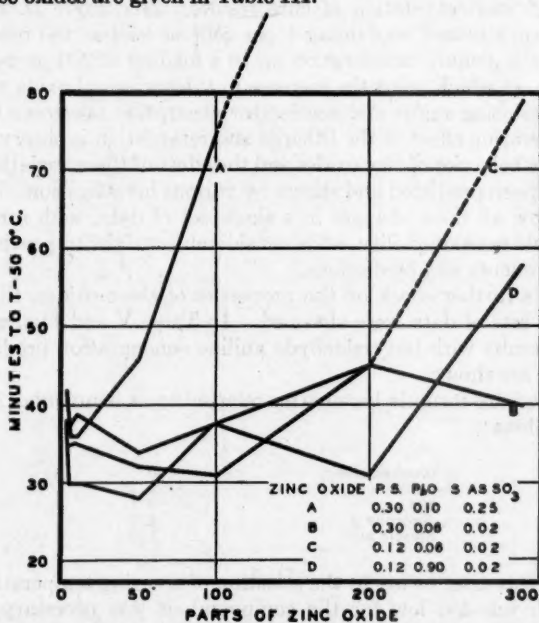


FIGURE 5. TESTS ON COMPOUND 2, 808

TABLE III. PROPERTIES OF ZINC OXIDES USED

Zinc Oxide	Particle Size Microns	Pb as PbO	S as SO ₃
A	0.30	0.10	0.25
B	0.30	0.06	0.02
C	0.12	0.06	0.02
D	0.12	0.90	0.02

The first series of tests was in a compound accelerated with mercaptobenzothiazole (Captax) and having the following base formula, hereafter referred to as compound 1:

Smoked sheet	100
Sulfur	3
Captax	1
Agerite powder	1
Stearic acid	3

The zinc oxide was varied from 2 to 300 parts on 100 parts of rubber. The results, expressed in the time required to reach a T-50 of -7.0°C. , are shown in Table IV and Figure 4.

Zinc oxide A, the "slow-curing" zinc oxide, shows a progressive retardation of cure as the amount of zinc oxide is increased, for with each increase in oxide content the amount of chemical retardant is increased. Zinc oxide B, the relatively coarse "fast-curing" zinc oxide, gives a straight-line relation, indicating that when the vulcanization reaction reaches an equilibrium there is no change in curing rate with a change in the zinc oxide loading. Zinc oxide C, the fine "fast-curing" oxide, because of its increased surface shows a slightly increased activity and speeding up of the cure to a loading of 50 parts of zinc oxide, at which point the sulfur and accelerator absorption causes an unbalancing of the compound and retardation of cure results. Zinc oxide D, fine particle size and containing 1 per cent of lead as the oxide, shows a definite acceleration up to a loading of 200 parts of oxide, at which point the increase in the surface of oxide and the resulting sulfur and accelerator absorption overcome the accelerating effect of the litharge and retardation is observed.

The behavior of zinc oxides and the effect of these variations have been predicted and shown by various investigations, but to show all these changes in a single set of data, with a reasonable reproducibility, adds considerable weight to previous experiments and predictions.

As a further check on the properties of these oxides, three other sets of data were obtained. In Table V and Figure 5, the results with butyraldehyde aniline condensation product (808) are shown.

The base formula hereinafter referred to as compound 2 is as follows:

Smoked sheet	100
Sulfur	3.25
808	0.7
Neozone A	1.0
Stearic acid	1.0

In this case, owing to the selection of a curing temperature which was too low for the compound, it was necessary to make the comparison at a T-50 somewhat higher than was used in the previously discussed tests. The value of 0°C. was selected and the conclusions were essentially the same as were reached in the mercaptobenzothiazole stocks.

Table VI and Figure 6 show the results with a combination accelerator, in this case benzothiazyl thiobenzoate (Ureka-C) and 2 diphenylguanidine, 1 phthalic acid, 1/2 water (Guantal).

The base formula hereinafter referred to as compound 3 is as follows:

Smoked sheet	100
Sulfur	3
Ureka-C	0.45
Guantal	0.30
Stearic acid	1

TABLE IV. TESTS ON COMPOUND 1, CAPTAX

Zinc Oxide	Cure at 126° C.	Parts of Zinc Oxide					
		2	5	10	50	100	200
Min.							
A	15	+ 8.0	+10.5	+10.0	+12.5	+13.0	+13.7
	30	-4.0	-1.0	+0.5	+2.0	+2.5	+0.6
	45	-13.5	-10.0	-8.0	-6.0	-4.5	-0.7
	60	-20.5	-15.5	-15.0	-12.5	-8.5	-5.5
	75	-25.0	-22.5	-20.5	-17.5	-15.0	-9.3
	10	+ 8.0	+10.5	+ 9.5	+10.0	+10.0	+13.0
B	15	+ 4.0	+6.5	+7.5	+7.0	+6.0	+7.0
	30	+7.0	-1.0	-2.0	-2.0	-3.0	+3.0
	45	-13.5	-11.0	-9.5	-9.0	-10.0	-8.0
	60	-19.5	-16.0	-15.0	-15.5	-15.5	-16.5
	75	-27.0	-25.0	-24.0	-19.5	-19.5	-19.0
	10	+ 9.5	+10.5	+ 6.5	+ 7.5	+ 8.5	+ 9.5
C	15	+ 6.5	+ 8.0	+ 6.5	+ 3.5	+ 3.0	+ 4.0
	30	- 5.5	- 3.0	- 4.0	- 6.0	- 4.0	- 5.5
	45	-12.5	-11.0	-10.5	-10.0	- 9.5	- 9.0
	60	-18.5	-17.0	-16.5	-14.0	-13.0	-11.5
	75	-24.0	-22.0	-21.0	-21.5	-19.5	-14.5
	10	+11.0	+11.0	+ 9.0	+ 7.5	+ 8.0	+10.5
D	15	+ 8.5	+ 6.5	+ 5.0	+ 4.5	+ 5.0	+ 3.5
	30	- 3.0	- 4.5	-11.5	-10.0	- 9.0	-10.0
	45	-10.5	-11.5	-16.0	-14.5	-14.0	-14.5
	60	-17.5	-17.0	-20.5	-19.5	-18.5	-18.0
	75	-22.0	-22.0	-20.5	-19.5	-18.5	-18.0
	10	+11.0	+11.0	+ 9.0	+ 7.5	+ 8.0	+10.5
Time of Cure (Minutes) to T-50 of -7.0° C.							
A	34	39.5	43.0	47.8	54.0	65.0	
B	32	35	38	41	38	37	
C	34	37	38	36	39	45	
D	37.5	36	35	36.5	39	34.5	
						53.5	

Time of Cure (Minutes) to T-50 of -7.0° C.

A
B
C
D34
32
34.5
37.539.5
35
37
3643.0
40
38
3547.8
41
36
36.554.0
38
36
3965.0
37
45
34.566.0
37
67.5
53.5

TABLE V. TESTS ON COMPOUND 2, 808

Zinc at Oxide	Cure 126° C.	Parts of Zinc Oxide					
		2	5	10	50	100	200
Min.							
A	10	+10.0	+9.5	+9.5	+8.0	+13.0	+21.0
	15	+8.0	+7.5	+8.0	+7.5	+12.0	+20.5
	30	+2.5	+2.0	+2.5	+4.0	+9.0	+17.5
	45	-1.5	-2.5	-3.0	-0.5	+4.5	+16.0
	60	-4.5	-6.0	-6.5	-3.5	+2.0	+13.0
	75	-8.0	-8.5	-9.5	-6.0	0	+10.0
B	10	+10.0	+10.5	+10.0	+9.5	+11.0	+15.5
	15	+8.0	+7.5	+9.0	+7.0	+9.0	+13.5
	30	+3.5	+2.0	+2.5	+1.0	+3.0	+5.0
	45	-1.5	-2.0	-3.0	-2.5	-3.0	-1.0
	60	-4.5	-5.5	-6.0	-7.0	-5.5	-4.0
	75	-10.5	-9.5	-11.5	-10.0	-9.5	-8.5
C	10	+10.0	+10.0	+12.0	+9.5	+8.5	+12.0
	15	+8.0	+7.5	+7.5	+7.0	+6.0	+15.0
	30	+3.5	+2.5	+2.0	+0.5	+4.0	+11.0
	45	-1.0	-2.0	-4.0	-4.5	-3.0	+3.0
	60	-7.0	-7.5	-7.0	-8.0	-7.5	+3.0
	75	-11.0	-11.0	-12.5	-11.5	-10.5	-3.0
D	10	+10.0	+10.0	+12.0	+9.5	+8.5	+12.0
	15	+8.0	+7.5	+7.5	+7.0	+6.0	+15.0
	30	+3.5	+2.5	+2.0	+0.5	+2.0	+5.0
	45	-1.0	-2.0	-3.0	-2.5	-3.5	-1.0
	60	-7.5	-8.5	-8.5	-7.5	-3.5	-4.0
	75	-11.0	-11.5	-11.5	-11.5	-6.5	-2.5
Time of Cure (Minutes) to T-50 of 0° C.							
A	41	36	36	46	75	45	
B	42	37	39	35	36	45	
C	38	35	35	32	31	45	
D	38	30	30	28	38	31	
						58	

Time of Cure (Minutes) to T-50 of 0° C.

A
B
C
D41
42
34
3836
37
35
3036
39
35
3046
34
32
2875
38
31
3845
40
79
58

Table VII and Figure 7 give the results with a thiazole zinc salt and Laurex (Z. M. L.).

The base formula hereinafter referred to as compound 4 is as follows:

Smoked sheet	100
Sulfur	3
Z. M. L.	1.95
B. L. E.	1
Laurex	0.5

In both these latter series, the same conclusions which were reached in the first series are confirmed.

Eliminating for the moment stocks with high zinc oxide loading and considering only those containing activation amounts of zinc oxide, some interesting comparisons can be made. In the compounds containing 5 and 10 parts of zinc oxides, while the differences are small and probably of little commercial significance, these differences are consistent. In every case, the slow-curing oxide, A, has the slowest rate of

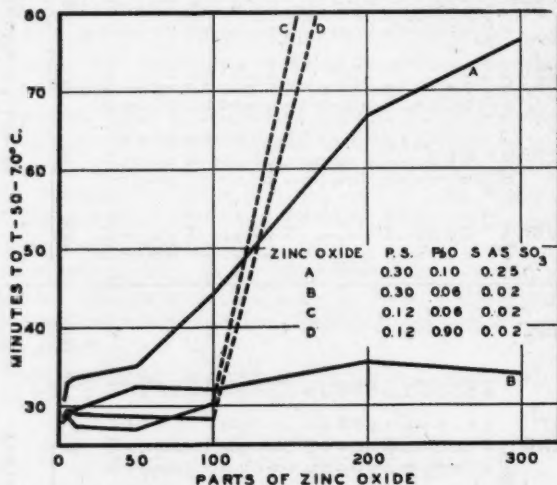


FIGURE 6. TESTS ON COMPOUND 3, UREKA C-GUANTAL

cure as judged by the T-50 test, being 5 or 6 minutes slower than zinc oxide D, which generally gives faster curing compounds. The spread between the extremes is somewhat greater in the case of the alkaline accelerators. These data are shown in Table VIII.

This conclusion being true for gum stocks, it was of particular interest to determine what differences could be detected in a loaded compound such as a tread stock. In Table IX are shown the results obtained in a typical tread stock accelerated with Captax and containing 40 parts of carbon black. Here the differences in zinc oxide are much less marked; in the case of 5 parts of pigment, zinc oxides A, B, and C are essentially equal, and zinc oxide D is only slightly faster. With 10 parts of zinc oxide, differences are noted which are not consistent with the observations made with the gum stocks.

TABLE VI. TESTS ON COMPOUND 3, UREXA C-GUANTAL

Cure at Zinc Oxide 130° C.		Parts of Zinc Oxide					300
Mins.		2	5	10	50	100	
A	15	+ 6.0	+ 7.5	+ 6.5	+ 8.5	+ 10.0	+ 14.8
	30	+ 6.5	+ 6.0	+ 5.0	+ 4.0	+ 1.0	+ 8.5
	45	-14.0	-13.5	-12.0	-11.5	-6.3	+ 3.0
	60	-18.5	-18.5	-18.5	-16.0	-5.5	-1.5
	75	-21.5	-22.0	-21.5	-19.5	-9.0	-6.5
	90	-23.0	-24.0	-24.0	-22.0	-11.0	-11.5
B	15	+ 6.0	+ 6.5	+ 5.0	+ 7.0	+ 8.0	+ 8.5
	30	+ 8.5	+ 8.0	+ 7.5	+ 5.5	+ 5.5	+ 3.5
	45	-15.0	-15.5	-14.5	-13.0	-13.0	-12.3
	60	-19.5	-19.5	-19.5	-18.0	-17.5	-18.5
	75	-23.0	-23.0	-22.0	-20.5	-21.0	-19.5
	90	-24.5	-24.5	-23.5	-23.0	-22.5	-21.5
C	15	+ 3.5	+ 3.5	+ 3.0	+ 2.5	+ 1.3	+ 8.5
	30	+ 7.5	+ 7.8	+ 7.5	+ 7.5	+ 8.3	+ 10.0
	45	-15.5	-15.5	-15.5	-16.0	-12.3	+ 5.0
	60	-19.8	-20.0	-20.8	-20.3	-16.0	+ 1.0
	75	-22.0	-23.0	-22.5	-22.0	-17.0	-2.0
	90	-23.5	-25.0	-24.3	-23.8	-18.0	+ 4.8
D	15	+ 4.8	+ 5.3	+ 3.0	+ 3.5	+ 1.0	+ 10.8
	30	+ 8.0	+ 8.5	+ 9.0	+ 7.3	+ 6.0	+ 10.5
	45	-14.3	-15.8	-15.8	-14.0	-13.3	+ 1.5
	60	-19.0	-20.5	-20.5	-18.5	-17.2	+ 3.0
	75	-22.3	-23.3	-22.0	-20.5	-19.3	-3.0
	90	-23.3	-25.5	-23.8	-22.3	-21.0	-4.3
Time of Cure (Minutes) to T-50 of -7.0° C.							
A	31	33	33.5	35	44.5	67.0	78.5
B	28	28	29.5	32.5	32.0	33.5	34.0
C	28.5	28.5	27.5	27.0	30.0
D	28.5	29.5	29	29.0	28.5

TABLE VII. TESTS ON COMPOUND 4, Z. M. L.

Zinc Oxide	at 135° C.	Parts of Zinc Oxide					Cure at 135° C.
		Mins.					
		2	5	10	50	100	
A	15	+ 3.5	+ 5.0	+ 4.5	+ 5.5	+ 5.0	+ 11.0
	30	+ 10.0	+ 9.5	+ 8.5	+ 6.0	+ 4.5	+ 10.5
	45	-21.0	-19.5	-18.0	-14.0	-12.0	+ 0.5
	60	-28.5	-25.0	-24.5	-21.0	-18.5	+ 8.5
	75	-38.5	-34.0	-31.0	-28.5	-25.5	+ 10.0
	90	-43.5	-37.0	-34.5	-31.0	-27.0	+ 13.0
B	15	0	+ 2.0	+ 2.0	+ 1.5	+ 3.0	+ 5.0
	30	+ 12.0	+ 11.0	+ 10.5	+ 9.5	+ 10.0	+ 7.5
	45	-22.5	-20.5	-19.0	-18.5	-16.0	+ 14.5
	60	-29.0	-26.5	-25.5	-23.5	-22.5	+ 19.5
	75	-36.5	-34.0	-33.0	-28.5	-27.5	+ 25.5
	90	-37.0	-33.5	-30.5	-29.0	-27.5	+ 25.5
C	15	+ 0.5	+ 1.0	+ 0.5	+ 1.5	+ 2.0	+ 14.0
	30	+ 11.5	+ 11.5	+ 12.0	+ 8.5	+ 6.0	+ 10.5
	45	-19.5	-20.0	-18.0	-16.0	-13.5	+ 6.0
	60	-25.0	-26.0	-22.5	-20.5	-18.0	+ 5.0
	75	-30.5	-31.5	-29.0	-26.0	-23.5	+ 1.5
	90	-32.5	-34.0	-31.5	-29.0	-26.5	+ 5.0
D	15	+ 3.5	+ 1.5	+ 1.5	- 0.5	- 1.0	+ 7.0
	30	+ 9.5	+ 12.0	+ 10.0	- 11.0	- 10.5	+ 10.5
	45	-19.0	-19.0	-18.5	-18.5	-15.5	+ 6.0
	60	-21.0	-24.0	-23.5	-22.5	-20.0	+ 1.5
	75	-33.0	-30.0	-28.0	-27.0	-25.0	+ 8.0
	90	-35.5	-32.5	-30.0	-29.5	-26.5	+ 9.0
Time of Cure (Minutes) to T-50 of -7.0° C.							
A	26	27.5	27.0	32.0	35.0	50.0	59.0
B	23	25	26	27.5	31.5	27	30.0
C	24	23.5	22.5	27.5	31.5	47	52.0
D	27.5	24	23.5	24.0	22.5

A similar set of tests with a compound loaded with whiting is shown in Table X. Here the differences in zinc oxides are about as well marked as they are in the case of the gum stocks, the oxides lining up in very much the same order. It would seem entirely likely that a compound extended with an inert pigment would show these differences, whereas a stock containing a pigment of high absorption characteristics might entirely mask the effect of differences in zinc oxides.

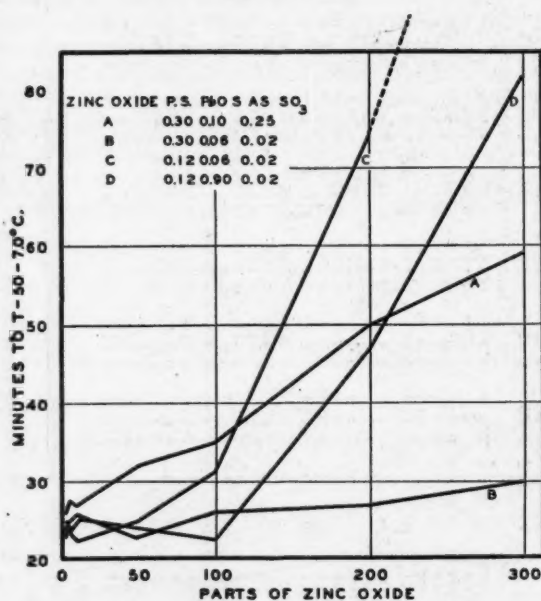


FIGURE 7. TESTS ON COMPOUND 4, Z. M. L.

TABLE VIII. GUM STOCK

(Minutes to T-50 of -7° C.)

Accelerator	5 Parts Zinc Oxide	Minutes to -7.0° C.	10 Parts Zinc Oxide	Minutes to -7.0° C.
Captax	B	35.0	D	35.0
	D	36.0	C	38.0
	C	37.0	B	40.0
	A	39.5	A	43.0
808	D	54.0	D	54.0
	C	58.0	C	54.5
	B	63.5	B	59.0
	A	66.5	A	62.0
Ureka C-Guantal	D	28.5	D	27.5
	B	29.0	C	29.0
	C	29.5	B	29.5
	A	33.0	A	33.5
Z. M. L.	C	23.5	C	22.5
	D	24.0	D	25.0
	B	25.0	B	26.0
	A	27.5	A	27.0

In discussing the data obtained with 808, it was pointed out that the results were considerably slower than those obtained with the other accelerators, because of the selection of a curing temperature that was too low for the compound. Another set of data using zinc oxide A, but curing at 142° C. rather than 126° C., was obtained and is shown in Table XI and Figure 8.

Although the time of cure to a T-50 of -7° C. may be the same in both compounds at the higher temperature, the ac-

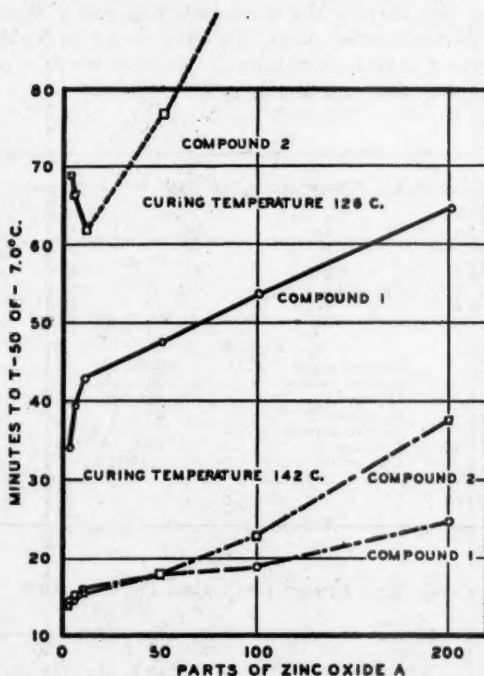


FIGURE 8. TESTS ON ZINC OXIDE A

TABLE IX. TREAD STOCK

5 Parts Zinc Oxide	Minutes to -7.0° C.	10 Parts Zinc Oxide	Minutes to -7.0° C.
D	75.0	D	74.5
A	88.0	B	83.5
B	88.0	A	85.0
C	88.5	C	88.0

Formula

Smoked sheet	100
Stearic acid	4
Pine tar	3
Carbon black	40
Captax	1.25
Sulfur	3
Zinc oxide	5 and 10

tual state of cure may be different. The interesting observation is that at this curing temperature the increase in zinc oxide content does not have the same retarding effect observed at the lower temperatures with either of these accelerators and it is only at the two higher loadings that any real differences can be observed.

A theoretical picture of the effect of the particle size of zinc oxide has been built up on the basis of accelerator and sulfur absorption. An extensive series of experiments has been carried out to demonstrate the correctness of these theories. By varying the accelerator and sulfur through a reasonable commercial range, the data shown in Table XII and Figure 9 have been obtained. For this series of experiments, Captax acceleration was again used.

TABLE X. COMPOUND LOADED WITH WHITING

5 Parts Zinc Oxide	Minutes to -7.0° C.	10 Parts Zinc Oxide	Minutes to -7.0° C.
<i>D</i>	32.5	<i>D</i>	29.0
<i>C</i>	33.5	<i>C</i>	34.0
<i>B</i>	35.0	<i>B</i>	34.0
<i>A</i>	39.5	<i>A</i>	40.5

Formula

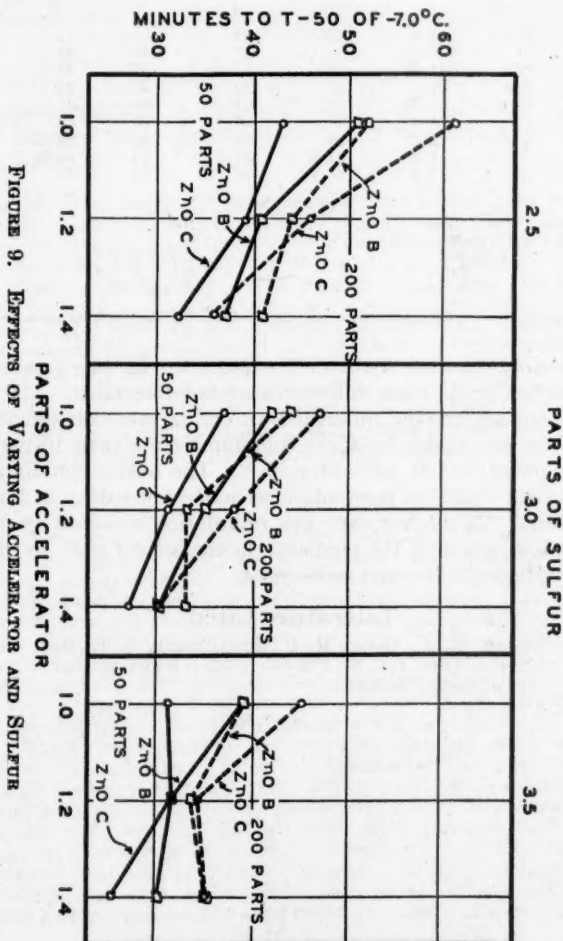
Smoked sheet	100
Sulfur	3
Captax	1
Stearic acid	3
Agerite powder	1
Whiting	67
Zinc oxide	5 and 10

TABLE XI. EFFECT OF CURING TEMPERATURE

	Curing Tempera- ture ° C.	Parts of Zinc Oxide <i>A</i>					
		2	5	10	50	100	200
Compound 1	142	14.5	14.5	16.0	18.0	19.0	25.0
	126	34.0	39.5	43.0	47.8	54.0	65.0
Compound 2	142	14.0	15.0	15.5	18.0	23.0	38.0
	126	69.0	66.5	62.0	77.0	100.0	174.0

It will be noted that at a loading of 50 parts of zinc oxide, zinc oxide *C*, the fine fast-curing oxide, is faster than the coarse fast oxide *B* when 1 per cent of accelerator is used. With 200 parts of pigment, the fine oxide is slower because of absorption of accelerator and sulfur as pointed out earlier. When the accelerator is increased to 1.4 parts, the fine oxide regains its faster curing rate. Increase in sulfur content has essentially the same effect to a less marked extent. When the amount of sulfur and accelerator is increased to an excess, the differences between the two oxides are masked.

In presenting the data in this paper, the authors do not pretend to have exhausted the possibilities of investigations by means of the T-50 tests. There are innumerable problems which suggest themselves, which will be studied, but it is felt



that the work has advanced to a point where the findings can be published and discussion of the method and data encouraged.

Conclusions

The T-50 test is an extremely satisfactory tool for the study of the curing rate of zinc oxides.

There are small differences in the curing rates of various zinc oxides when used in activation amounts in gum stocks

TABLE XII. EFFECT OF VARIATION OF SULFUR AND ACCELERATOR

(In compounds containing 50 and 200 parts of zinc oxides *B* and *C*)

Parts Sulfur	Parts Accelerator	Minutes to -7.0°C. at T-50			
		50 parts zinc oxide		200 parts zinc oxide	
		<i>C</i>	<i>B</i>	<i>C</i>	<i>B</i>
2.5	1.0	43	51	61	52
	1.2	39	41	46	44
	1.4	32	37	36	41
3.0	1.0	37	42	47	44
	1.2	31	35	38	33
	1.4	27	30	30	33
3.5	1.0	31	39	45	39
	1.2	31.5	31.5	34	33.5
	1.4	25.0	30	35	35

Formula

Rubber	100
Stearic acid	3
Sulfur	2.5-3.0-3.5
Captax	1.0-1.2-1.4
Zinc oxide	50 and 200

and stocks loaded with inert extenders. In the presence of carbon black, these differences are not detectable.

There are marked differences in curing rate between the various zinc oxides in stocks containing more than 10 parts of pigment in 100 parts of rubber. The oxides containing sulfur show marked retardation, as do the fine oxides, at high loadings. In the first case, this retardation is caused by the chemical nature of the pigment; in the second case, by the absorption of sulfur and accelerator.

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The Goodrich Flexometer

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THE service of rubber compounds often is limited by the heat generated during the flexing of the rubber and several types of flexing machines have been developed to study this factor.

In one of the first tests (14) devised, a spherical test piece was rotated under compression between two parallel plates until rupture occurred. Vogt (20) described the use of the Shields rotary machine. In this test bands are stretched radially over lubricated pins on a vertical rotating disk. The center pins are on an eccentric so that the bands are alternately stretched and relaxed. The hysteresis is measured by the throw of a pendulum which measures the torque produced. Later Abbott (1) arranged test pieces between two horizontal plates. The loaded top plate was then oscillated in the horizontal plane. The flexure-set, temperature rise, and time of failure were observed. Depew and Snyder (8) subjected rubber cylinders to a specified number of hammer blows per minute in order to study heat generation and breakdown.

In 1933, Cooper (5) reported a new compression flex test in which the test piece was held between two loaded, eccentric horizontal plates, one of which was rotated usually until the sample ruptured or blew out. (For those unfamiliar with the terminology of the rubber industry it should be stated that blow-outs in solid masses of rubber are caused by the development of high temperatures at the center of the mass, causing decomposition, the formation of liquid and gaseous compounds, and finally rupture of the solid walls of the mass by the expansion of these decomposition products. In large masses under heavy loads the temperatures attained have been so high that ignition of the gases has occurred spontaneously.) The changes in the test piece during the test were followed by measuring the permanent set. Havenhill and MacBride (11) in 1935 described an improved compression flexometer fundamentally similar to Cooper's machine, but so designed that the horizontal forces necessary to displace or maintain the lower plate in a given off-center position could be measured at any time. With this arrangement certain structural changes during flexure could be followed. In later experiments Havenhill (10) showed that rubber test pieces stiffened during flexure and in some instances exhibited an anisotropic structure.

The development of these tests has moved in the direction of smaller and more conveniently prepared test pieces, but none of them has reached the stage where the test pieces were small enough to be cut from finished products such as pneumatic tire treads, nor could they be used very effectively with rubber-fabric compositions. In the tests which employ the off-center rotation, large horizontal forces are encountered which act in opposite directions at the two plates and large loads are required to keep the test pieces from slipping. For this reason the specimens usually develop very high tem-

peratures and blow out in a very short time. Apparently none of the tests has been used generally to measure the temperature rise at equilibrium under less severe flexing conditions, nor have the machines so far described been equipped for work at elevated temperatures.

The study of ply separation or the separation of fabric from rubber has been confined, for the most part, to the study of belts (12, 16) driven under load or to strips of plied, calendered fabric subjected to a reciprocating motion (7, 9, 13, 18) over a pulley. Flex tests designed to test tread-cracking have been used to some extent to evaluate ply separation in plied fabric samples (17, 19). The essential characteristics of the

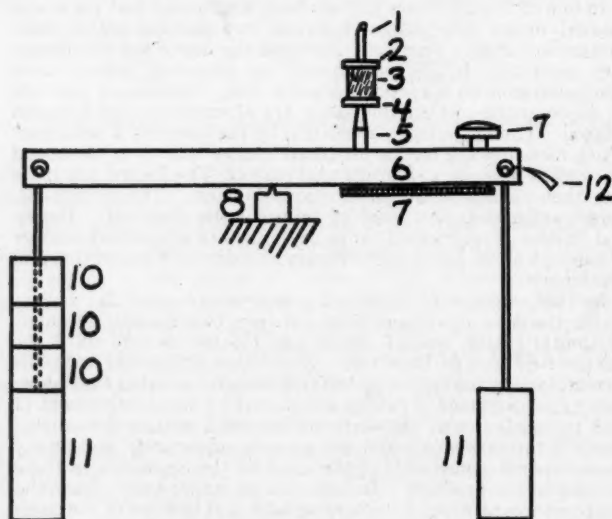


FIGURE 1. DIAGRAM OF FLEXOMETER

different types of flex tests have been summarized in several publications (2, 3, 6, 15).

A new form of hysteresis test has been developed in this laboratory and used for a number of years here and in several other laboratories in the study of both rubber and rubber-fabric compositions at ordinary and elevated temperatures. It involves applying a definite compressive load to the bottom face of a test piece through a lever system having a high inertia, imposing on the upper face of the sample an additional high-frequency cyclic compression of a definite amplitude, and measuring with a thermocouple the temperature rise at the base of the sample. Because of the high inertia and low natural period of the lever system, practically none of the high-frequency vibration is transmitted to the loading lever, although the lever does move to compensate for the slow changes in the sample caused by permanent set and other

structural changes. Light loads and high-frequency vibrations of low amplitude cause the temperature to rise to some equilibrium value; heavier loads and larger deflections produce a complete breakdown on the sample. Samples may be tested under a constant applied load, a constant initial compression, or at constant deflection during the test. The change in height of the test piece can be measured continuously during flexure and the degree of softening or stiffening, the effect of anisotropic differences in structure or modulus changes over

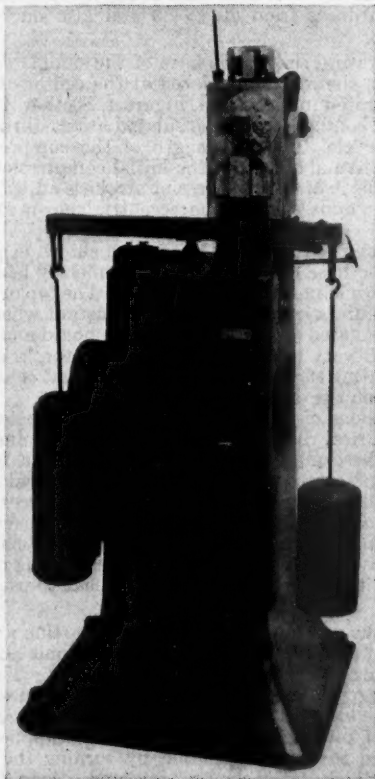


FIGURE 2. PHOTOGRAPH OF
ASSEMBLED MACHINE

a range of temperatures can also be observed. The test piece is of a convenient size so that test specimens may be obtained directly from manufactured articles.

Description of the Machine

The assembled machine¹ is shown in Figure 2 and the essential parts of the system are sketched in Figure 1 and may be described briefly as follows:

¹ These machines may be obtained from the Ferry Machine Co., Kent, Ohio.

The test piece, 3, is placed between anvils covered with hard rubber, 2 and 4. The top anvil, 2, is connected through 1 to an adjustable eccentric usually driven at 1800 r. p. m. The load, 10, is applied by means of the lever, 6, resting on knife-edge 8. The moment of inertia of the lever system is increased and its natural frequency reduced, by suspending the equal weights, 11, 11, at each end of bar 6 at positions equidistant from the knife-edge. Anvil 4 can be raised and lowered relative to bar 6 by means of a calibrated micrometer device, 7, 7. With this device the bar may be maintained in a horizontal position during a test, as indicated by pointer 12 and a reference mark on the bar. The dimensions indicated in the legends of Figures 3 and 4 have proved satisfactory for tests on rubber samples of any Shore durometer hardness from 20 to 80 and also on rubber-fabric samples.

The temperature rise at the base of the sample is determined by means of a thermocouple placed at the center of the bottom anvil as illustrated in position 6, Figure 4, Section A.A. To keep the sample in contact with the insulated anvils during the entire compression cycle, the total length of the compression stroke must be less than about twice the initial compression of the test piece. The length of the compression stroke is adjusted by means of the vernier and scale on the eccentric shown in position 8, Figure 3.

The machine is equipped with an oven shown in position 1 in Figure 3. The base of the oven is permanently fastened to the frame, as shown in position 8 of Figure 4. The top or oven proper slides in place and can be removed in an instant when not in use. The oven is insulated with 0.5-inch asbestos board and is equipped with two 125-watt heaters, a thermoregulator, a squirrel-cage fan for circulating the air, and a small light that is automatically turned on when the oven door is open.

The dimensions of the machine have been selected to accommodate cylindrical rubber test pieces 1 inch high and 0.7 inch in diameter. These may be conveniently cut from larger blocks or from manufactured articles, using a cylindrical cutting tool either in a drill press or lathe. Laminated test pieces also may be built up without the use of adhesive from thin disks 0.7 inch in diameter arranged horizontally in the machine. Smaller or larger test pieces may be used if necessary. When testing rubber-fabric compositions it is sometimes more convenient to use rectangular samples.

To adjust the micrometer device before starting a test, the top anvil is raised as far as the eccentric will permit and a piece of brass 1 inch high is inserted between the plates. The calibrated micrometer is set at zero and the pointer, 12 (Figure 1), is set on a mark on the end of the lever bar to locate the zero position. When the test piece is inserted and the load applied the bar is again returned to its zero position by turning the micrometer mechanism. The static compression under load is then read directly on the micrometer scale to 0.001 inch.

The lever bar is adjusted to zero position at intervals to determine the change in the mean height of the sample during flexure. The permanent set is taken as the per cent difference in height between the original unstressed test piece at room temperature and the height of the unstressed test piece at room temperature after flexure, referred to the original height.

The temperature rise, measured at the base of the sample, depends not only upon the heat generated, but also upon the conductivity and emissivity of the test piece, the conductivity of the insulators, etc. If necessary, the observed temperatures may be corrected for differences in conductivity, but in practice this and other corrections may be neglected and the stocks compared on a basis of actual temperature rise at the base of the test

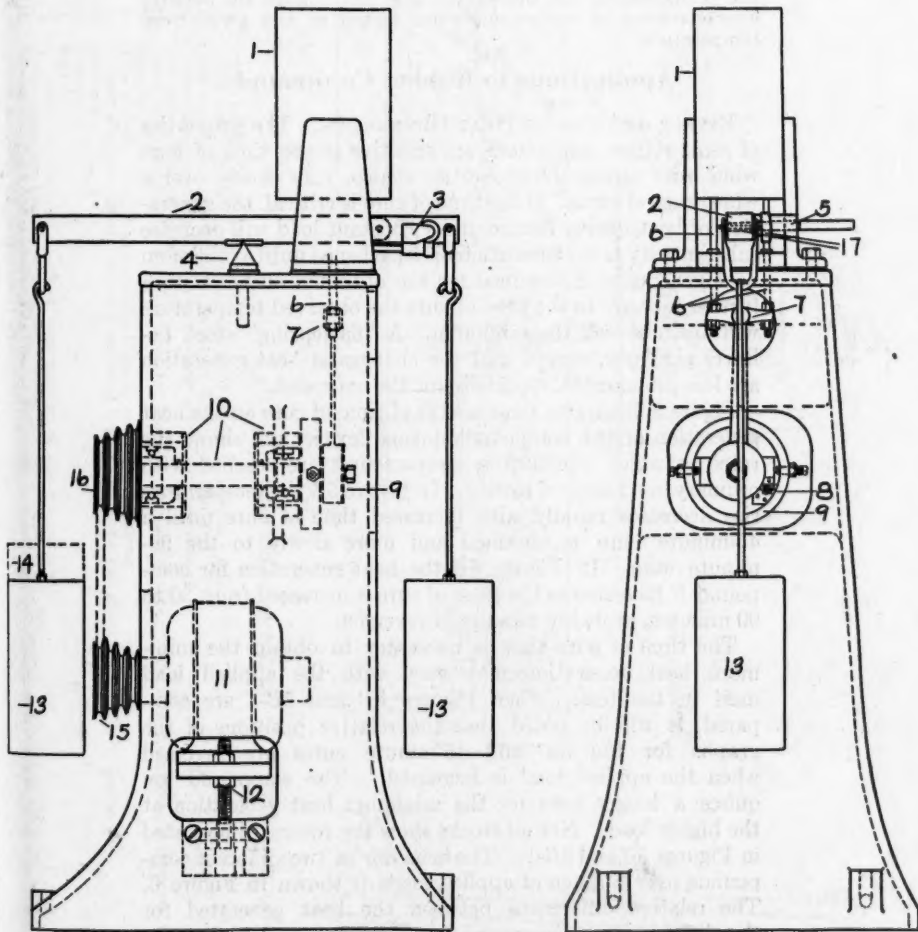


FIGURE 3. SIDE AND FRONT VIEWS

1. Oven, thermostatically controlled
 2. Balance bar, $24 \times 1.5 \times 1.5$ inches
 3. Mechanism for raising and lowering bottom anvil with accessory mechanism to read this movement to 0.001 inch
 4. Fulcrum, a knife-edge on which 2 is balanced
 5. Tapered rod by means of which 2 may be held in position to avoid initial impulse when motor is started
 6. Rods connecting upper anvil to driving mechanism
 7. Bearing and connecting rod to eccentric
 8. Vernier and scale for gaging eccentricity
 9. Housing for eccentric
 10. Shaft and bearing to rotate eccentric
 11. Motor
 12. Mechanism for adjusting height of motor and tension on belt
 13. Inertia weights (50 lb.)
 14. Load
 - 15, 16. Pulleys arranged to give four speeds
 17. Calibrated mechanism for reading height of bottom anvil relative to a reference point
- Distance between points of suspension of inertia weights and fulcrum is 11.35 inches and distance between loading platform and fulcrum is 5 inches.

piece. The amount of heat lost through the insulators varies with the temperature, but this factor does not change the relative characteristics of compounds when tested at any given oven temperature.

Applications to Rubber Compounds

EFFECT OF CURE ON HEAT GENERATION. The properties of some rubber compounds are sensitive to the time of cure while with others the properties change very slowly over a wide range of cures. If the time of cure is critical, the generation of heat during flexure under constant load will decrease substantially as the time of cure is lengthened until a minimum heat generation is obtained for the optimum cure. With a further increase in the time of cure the observed temperature will again exceed the minimum. A "flat-curing" stock behaves similarly, except that the changes in heat generation are less pronounced, especially for the overcures.

Figure 5 illustrates some effects of time of cure on the heat generation of two compounds during flexure, and shows the rates at which equilibrium temperatures are reached with ordinary conditions of testing. In Figure 5A the temperature rise decreases rapidly with increased time of cure until a 45-minute cure is obtained and more slowly to the 90-minute cure. In Figure 5B the heat generation for compound B increases as the time of cure is increased from 30 to 90 minutes, probably because of reversion.

The time of cure that is necessary to obtain the minimum heat generation may vary with the applied load used in the test. When Figures 5B and 5B-1 are compared, it will be noted that the relative positions of the graphs for the 30- and 45-minute cures are reversed when the applied load is increased. The compound requires a longer cure for the minimum heat generation at the higher load. Not all stocks show the reversal illustrated in Figures 5B and 5B-1. The behavior of two different compounds over a range of applied loads is shown in Figure 6. The relative differences between the heat generated for the different cures increase as the load is increased but the relative order is unchanged. For these compounds the temperature rise for the overcure is only slightly higher than for the optimum cure.

EFFECT OF PIGMENTATION. The graphs in Figure 7 illustrate the nature of the temperature curves obtained with stocks containing 0 to 30 parts by volume of carbon black on 100 of rubber with 3.5 parts of sulfur and 6.0 parts of litharge, cured 75 minutes at 280° F. Litharge was used as an accelerator because it gives the same rate of cure with different amounts of black.

The test pieces, 1 inch high by 0.7 inch in diameter, were flexed at room temperature under an applied load of 140 pounds per square inch and a compression stroke of 0.175 inch. The temperature rise varied from 27° F. for the gum stock to

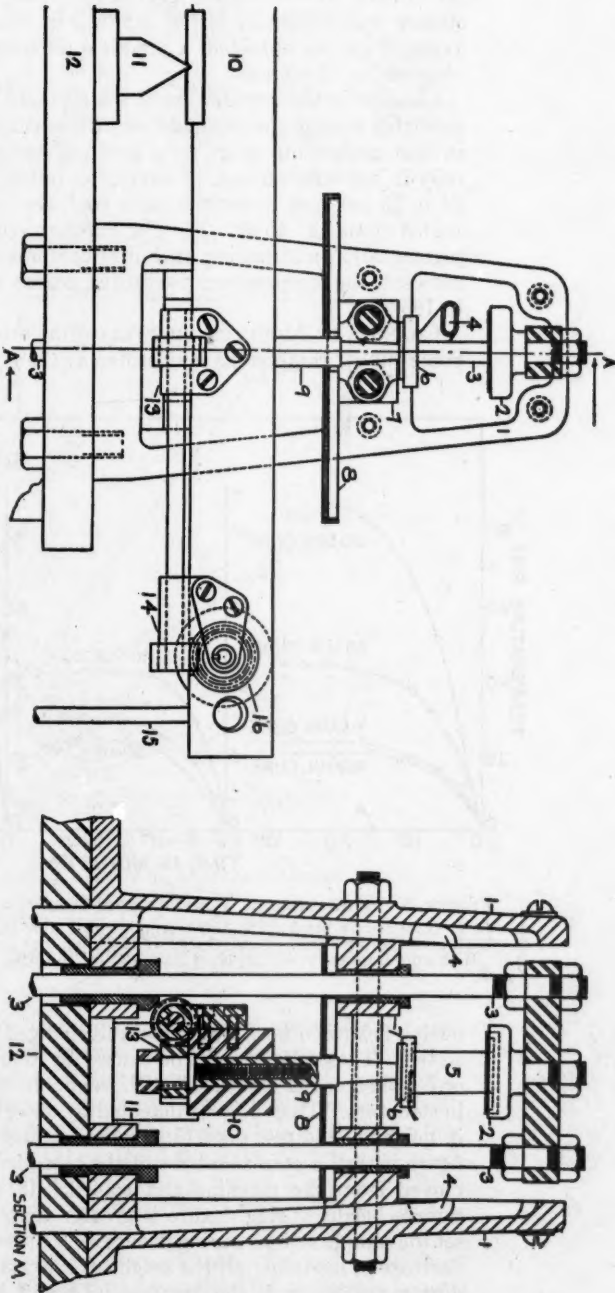


FIGURE 4. SIDE AND FRONT VIEWS WITH OVEN OMITTED

1. Frame holding bearings and oven
2. Upper anvil driven through rods; 3: hard-rubber insulation 0.1 inch thick
3. Rods connected to eccentric as shown by 6 and 7 in Figure 3
4. Concealed air vent for producing windage or cooling when desired
5. Test piece (Section A-A)
6. Lower anvil showing hard-rubber insulator 0.1 inch thick and showing position of thermocouple (Section A-A)
7. Bearing
8. Base of oven. Entire oven can be lifted from base at any time
9. Support for lower anvil. Anvil is raised or lowered by screw and gears 13, 14
10. Inertia bar
11. Fulcrum
12. Frame
13. Gears by means of which vertical position of 9 or 6 is adjusted
14. Rods supporting inertia weights
15. Mechanism for turning gears 13 and 14. Calibrated to read height of sample to 0.001 inch from zero point level of bar. Zero point indicator omitted here is shown, 12, in Figures 1 and 2.

90° F. for the 30-volume gas black stock. Although the flexure was continued for 80 minutes in order to show the types of graphs obtained, a practical differentiation may be obtained in 25 minutes.

Changes in the formulation of a compound that do not appreciably change the hardness may cause substantial changes in heat generation—e. g., for a group of compounds differing only in acceleration and all having an initial compression of 24 to 25 per cent under the same load, the temperature rise varied from 13° to 52° F. For another group differing in pigmentation and having an initial compression of 15 to 17 per cent, the temperature rise during flexure varied from 98° to 165° F.

CHANGES IN MODULUS OR STRUCTURE DURING FLEXURE. Some rubber compounds may stiffen as the temperature rises

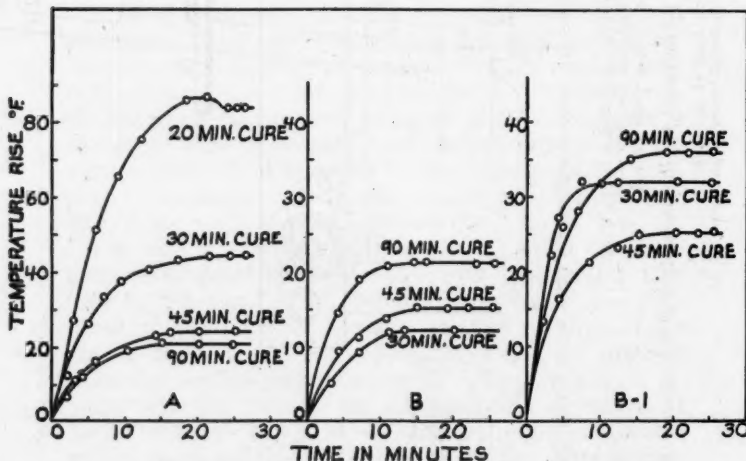


FIGURE 5. VARIATION IN TEMPERATURE RISE WITH CURE AND LOAD

- A. D. P. G., 9 carbon black, 15% ZnO. Applied load of 62 lb./sq. inch
 B. High gum-Captax stock. Applied load of 62 lb./sq. inch
 B-1. High gum-Captax stock. Applied load, 122 lb./sq. inch. Compression stroke, 0.25 inch

during flexure, others may remain unchanged, and some may soften. These effects may be caused by thermal expansion, or by phenomena associated with the Joule effect or changes in structure. They may be detected by observing the change in height of the test piece during flexure and comparing this figure with the permanent set of the test piece after it is removed from the machine and cooled. If the decrease in sample height during flexure is greater than the permanent set the sample softens during flexure—i. e., there is a reversible decrease in modulus. If the height of the test piece increases during flexure, or if the decrease in height is less than the permanent set, the compound stiffens during flexure.

TABLE I. EFFECT OF CARBON BLACK LOADING ON STRUCTURE AND HEAT GENERATION DURING FLEXURE

Compound	Volume Loading of Gas Black	Temperature Rise during Flexure	Change in Height during Flexure	Permanent Set	Increase in Height Caused by Reversible Structural Changes
		$^{\circ}\text{F.}$	$\%^a$	$\%^a$	$\%^a$
A	0	27	+1.0	1.1	2.1
B	10	37	+0.6	1.4	2.0
C	20	56	-1.0	3.1	2.1
D	30	89	-6.2	8.8	2.6

^a Based on initial height of test piece.

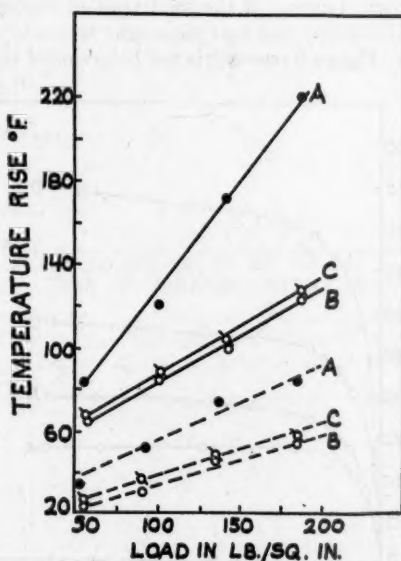


FIGURE 6. EFFECT OF APPLIED LOAD ON TEMPERATURE RISE

A, 60-minute cure; B, 110-minute cure; C, 160-minute cure
 — 50% carbon black stock
 - - - 5% zinc oxide stock

The changes in height during flexure observed for the carbon black stocks mentioned above are graphed in Figure 8 and are compared to the permanent set in Table I. All the data are expressed as per cent change based on the initial height of the uncompressed test piece. For compound D in Table I, the permanent set is 8.8 per cent, while the recorded decrease in height during flexure is only 6.2 per cent. The height during flexure was, therefore, 2.6 per cent greater because of a reversible increase in modulus.

All these compounds stiffen slightly. By way of further illustration these effects may be noticed for the several compounds listed in Table II.

TABLE II. STRUCTURAL CHANGES IN SEVERAL COMPOUNDS DURING FLEXURE

(Flexed 75 minutes under an applied load of 155 pounds per square inch)

Pigment Loading	Change in Height during Flexure %	Permanent Set %	Modulus Changes during Flexure
1. Gas black 20%, whiting 15%, tire reclaim 18%	-25	20	Softens
2. Gas black 4%, clay 28%, reclaim 20%	-34	46	Stiffens
3. Zinc oxide 19%, soft black 16%, whiting 37%	- 2.5	3.7	Not much change
4. Zinc oxide 4%	+ 2.5	0.0	Stiffens

BREAKDOWN TESTS. If the load applied during flexure is increased sufficiently, the test piece may be made to blow out or fracture. Figure 9 represents the behavior of two different

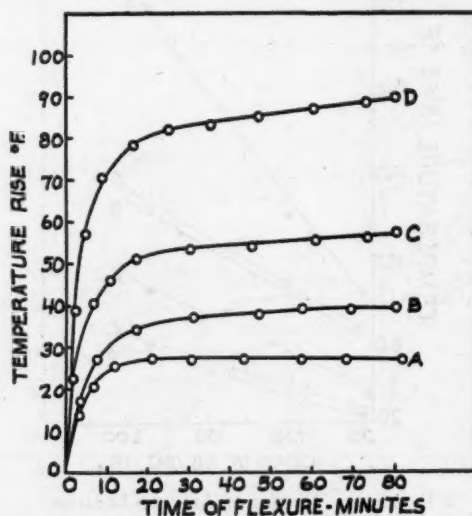


FIGURE 7. TEMPERATURE RISE USING VARIOUS PERCENTAGES OF CARBON BLACK

Volume loading: A, 0%; B, 10%; C, 20%; D, 30%

rubber compounds under identical testing conditions. Compound A blew out in 60 minutes, while compound B was in excellent condition even after 150 minutes of flexure. The primary inflection point observed for compound A has been of no practical importance for comparing breakdown characteristics of rubber compounds and may be entirely absent when the test is greatly accelerated or when reversion does not occur.

Some types of pigmentation produce stocks that run cooler during flexure but are mechanically weaker than stocks that revert. These stocks may break down or crumble under high loads. It is therefore important that the loads used in testing such stocks should be of the same order of magnitude as those

encountered in service, allowing for a reasonable factor of safety. It has been reported (4) that the time of "blowout" of

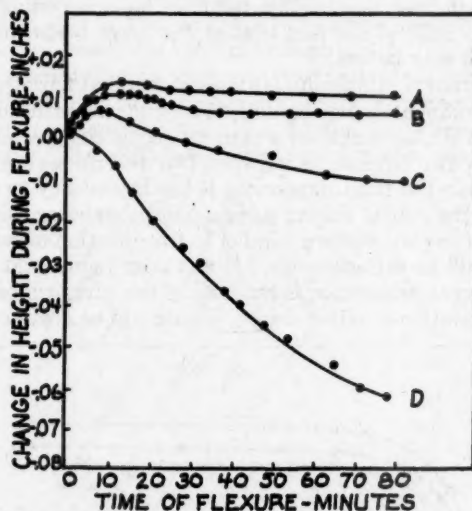


FIGURE 8. CHANGE IN HEIGHT OF FLEXURE USING VARIOUS PERCENTAGES OF CARBON BLACK
Volume loading: A, 0%; B, 10%; C, 20%; D, 30%

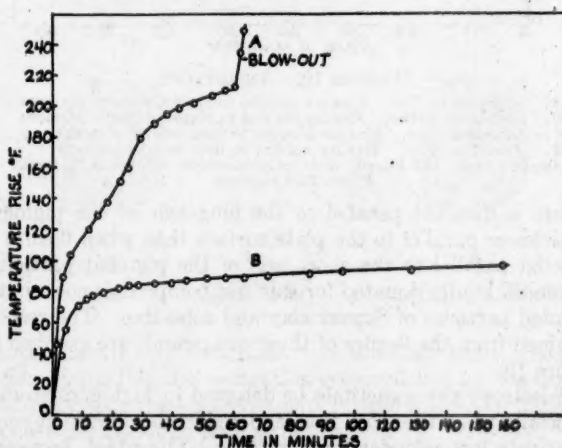


FIGURE 9. FATIGUE TEST

A. Loaded with channel black, 25 parts, and zinc oxide, 132 parts
B. Loaded with soft black, 51 parts, and zinc oxide, 10 parts
Applied load: 180 lb./sq. inch. Compression stroke, 0.25 inch

rubber compounds is related to the hysteresis of the compound or the heat generated during flexometer tests. There are,

however, exceptions in practice because of the different types of fracture possible. If, as mentioned above, the compound fractures without reverting, the time to produce breakdown under high load may be shorter than for a reverting compound in spite of the fact that at the lower loads the heat generated may be less.

ANISOTROPY. Havenhill (10) has shown that anisotropy in rubber compounds can be detected by means of flexometer tests. When the length of a pigment particle is greater than the other two dimensions, or when two dimensions are much larger than the third dimension, it has a tendency to orient itself in the rubber during mixing and calendering with the long axis or plate surface parallel to the direction of rotation of the mill or calender rolls. It has been found that when this pigment orientation is retained in the cured rubber, the heat generation obtained during flexing will be greater if the

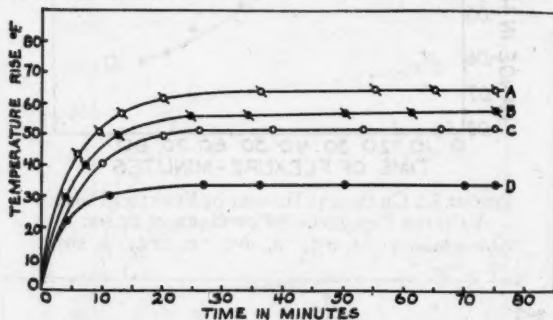


FIGURE 10. ANISOTROPY

- A. Suprex-clay filler. Flexure parallel to plate surface of pigment
 B. Suprex-clay filler. Flexure normal to plate surface of pigment
 C. Asbestine filler. Flexure parallel to long axis of pigment
 D. Asbestine filler. Flexure normal to long axis of pigment
 Applied load, 143 lb./sq. inch. Compression stroke, 0.25 inch.
 Filler, 25.6 volumes

flexure is directed parallel to the long axis of the pigment particles or parallel to the plate surface than when flexure is directed parallel to the short axis of the pigment particles. Havenhill kindly donated for this test compounds containing oriented particles of Suprex clay and asbestine. The results obtained from the flexure of these compounds are graphed in Figure 10.

Anisotropy can sometimes be detected in high-gum stocks, especially when the stock is calendered in thin sheets at comparatively low calender temperatures. The effect, however, is usually small and may be eliminated by holding the stocks at an elevated temperature before they are cured, for a time dependent upon the degree of anisotropy that may occur.

Applications to Rubber-Fabric Compositions

When rubber-fabric compositions are constructed so that a definite angle is obtained between cords in alternate plies, test pieces may be cut from the cured composition in two

directions as indicated in Figure 11A. The flexure characteristics of these test pieces may then be compared for different rubber compounds. If any cord angle other than 90° is chosen, one test piece may be obtained having cord angles of less than 90° as in Figure 11B, and another may be obtained having cord angles greater than 90° as in Figure 11C. The tendency for cord separation in the type C test piece is greater than for type B because the compressive force causes a greater strain between cord and rubber. This type of test piece is useful in studying the resistance to cord separation in compositions

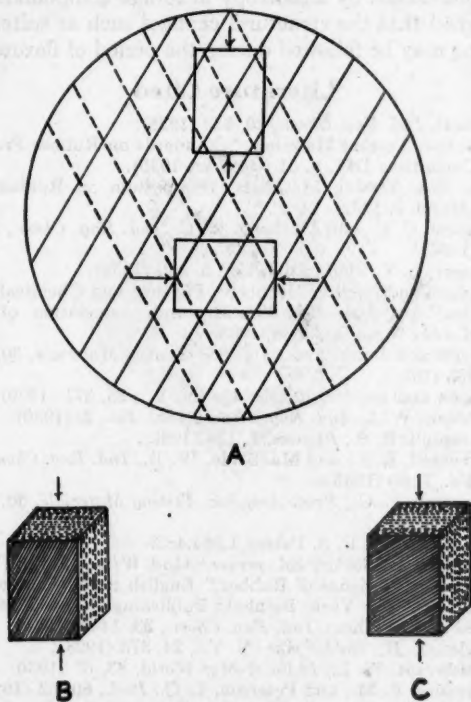


FIGURE 11. APPLICATION TO RUBBER-FABRIC COMPOSITIONS

having similar cord structures. On the other hand, since the tendency for the cord separation is diminished for the type B test piece, this type is more useful for the study of differences in heat generation in such structures.

The study of rubber-fabric compositions may follow the same procedure as for rubber compounds. Tests may be made to produce equilibrium temperatures or the load may be increased to produce breakdown. The test pieces may be subjected to a constant applied load, or, when comparing a series of compositions, the load may be adjusted from one composition to the other in order to obtain compressions of similar magnitude.

Summary

The Goodrich flexometer is of simple design and is easily operated at ordinary or elevated temperatures. Test pieces procured from laboratory specimens or from finished rubber or rubber-fabric products may be tested, using moderate loads that produce equilibrium temperatures during flexure or larger loads that rupture the test piece. This machine may be used to study the effects on heat generation of the time of cure, the magnitude of the applied load, changes in pigmentation, and variations caused by anisotropy in rubber compounds. It is so designed that the structural changes such as softening or stiffening may be followed during the period of flexure.

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